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PRESIDENT'S COLUMN

Indian Mining Industry, which has got several setbacks since recent past, is one of the main contributors to GDP contributing for about 2-3%. Producing more than 85 minerals, India ranked 4th in iron ore, 6th in bauxite and manganese, 10th in Alumina and 11th in crude steel. Importance is given now for value addition in sustainable mining and in mineral processing industries. Owing to an increase demand and need of steel for infrastructural development, coupled with export requirement of iron ore fines, the growth in iron ore development has witnessed exponential growth since last decade. In a view to meet the demand, the iron ore industries geared up to enhance the production over and above the prescribed limit as mentioned in various statutory proposals. This has prompted the various regulatory agencies of state and central governments to proactively monitor the compliances of all statutory provisions. Ministry of Mines, Govt. of India has also constituted Justice M.B. Shah Commission to inquire into these irregularities. The commission started functioning under certain terms of references and examined the various mining issues with special reference to increase in production of iron ores in Goa, Karnataka, and Odisha, which is still in progress. Setting and functioning of this commission has created a fear complex within all mining related officials of three states. This has naturally deterred the development of mineral resources in the states. The crux of the problem is the absence of any competent mining professionals in the commission and this will surely jeopardize the findings related to mineral development. We all agree that mining is a dynamic process and during operation it is very impracticable to maintain the production norms as indicated in the statutory documents. One should not give importance to this lacunae as there exist provisions to modify the statutory documents and this should not be termed as illegal mining. Mining professionals should unitedly raise their voices in different forums through their professional societies to curb this mis-propagation. Organising seminars/symposia only shall not help to overcome this situation; rather a consistent and continuous proactive deliberations and interaction with the concerned regulatory bodies should be attempted by the mining professionals.

Let good sense prevail with the professionals to fight for this noble cause which would help in mineral resources development a vital necessity for country's economic growth.

Dr. S.K. Sarangi
President

EDITORIAL REMARKS

WE ALL ARE AWARE OF THE FACT THAT **SOCIETY OF GEOSCIENTISTS AND ALLIED TECHNOLOGISTS (SGAT)** IS PUBLISHING A BIANNUAL BULLETIN SINCE LAST 13 YEARS AND HAS SO FAR PUBLISHED 25 VOLUMES. SGAT BULLETIN HAS ALSO GOT ISSN 0972-2173. A BULLETIN CAN BE PUBLISHED REGULARLY WITH IMPROVED QUALITY WITH THE CONTINUED SUPPORT OF READERS BY CONTRIBUTING SUITABLE ARTICLES.

IN SPITE OF REPEATED REQUEST AND REMINDERS, MEMBERS AND READERS ARE NOT MAKING SERIOUS ATTEMPTS TO SEND ARTICLES FOR WHICH THE BULLETIN COULD NOT BE PUBLISHED IN TIME. CAN THIS BULLETIN, A MOUTHPIECE OF SGAT, SUSTAIN WITHOUT THE BENEVOLENT SUPPORTS OF THE MEMBERS AND READERS?

SGAT, BEING AN INSTITUTION WITH ALL LEARNED MINING PROFESSIONALS SHOULD NOT FACE THIS UNFORTUNATE SITUATION.

MY APPEAL TO ONE AND ALL IS TO CONTRIBUTE ARTICLES REGULARLY FOR THE SUSTENANCE OF THIS BULLETIN, WHICH IS NORMALLY PUBLISHED IN DECEMBER AND JUNE EVERY YEAR.

THANKS AND WISH YOU ALL A HAPPY AND PROSPEROUS NEW YEAR – 2013.

DR. S.K. SARANGI
EDITOR, SGAT BULLETIN

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FLOTATION STUDIES ON TAILINGS FROM COKING COAL WASHERY

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ABSTRACT

In the present study, the coking coal washery tailings generated by the flotation circuit of one of the washeries in Eastern India were collected and used for this investigation. Attempts have been made to recover the additional clean coal from these tailings. As received tailings sample contains around 0.7% moisture, 19.1% volatile matter, 41.8% ash and 38.4% fixed carbon. The characterization study reveals that quartz is the major gangue mineral followed by kaolinite. Beneficiation study by both conventional cell and column flotation has been carried out to examine the maximum possibility of reducing the ash content. Studies have been conducted at different operating conditions. By three stage conventional cell flotation studies, it is possible to a get clean coal with 14.23% ash at 17.76% yield and 26.17% combustible recovery. Another 2% in yield has been improved by using Nalco reagent in place of MIBC as a frother. Further the ash can be reduced up to 13.56% at 21.03% yield by two stage column flotation studies. Release analysis was carried out to evaluate the performance of the coal tailings flotation.

Keyword: Coking coal; tailings; cell flotation; column flotation; combustible recovery.

INTRODUCTION

Amongst other natural resources, coal occupies the key position as a major resource of commercial energy and plays a major role in economic development of India with particular reference to metallurgical and energy sectors. The demand of coal in India is mostly dependent on the production of steel, cement and power. In addition to above which together account for about 86% of the demand, fertilizer and other sector consumes the rest of the coal production. It is apparent that the gap between the demand and production will keep on widening. A number of utilities have started importing the quality coal to meet the requirement, which indicates that there is gradual increase in import due to reduction in duty on import and non availability of better quality coal from India. Some industries are adopting blending of imported coal with domestic coal to improve the quality [1-2].

India is contemplating to produce 110 MT of finished steel by 2020, which requires quality raw material such as iron ore, fluxes and almost equal quantity of coking coal. Every effort should be made to utilize the available resources properly. Indian coking coal is inferior in quality and needs washing prior to utilisation. Lot of washeries were eshtablished to improve the quality of coking coal. These washeries are not giving desired performance due to change of raw materials and presence of near gravity materials. Lot of good coal is being lost in tailings as rejects [1, 3].

The normal practice of washing coking coal in India is to crush raw coal to finer sizes (preferable –13 mm) and is classified at 0.5 mm size. The coarse fraction is treated by using heavy media bath or cyclone. Below 0.5 mm size fraction in form of slurry is treated in flotation circuit to improve the quality of the coal fines. During washing, lot of coking coal is being discarded as tailings. The tailings contain lot of carbon values. A key element in process selection is maximum recovery of the product from raw coal at lowest possible cost. Maximization of the recovery of clean coal at desired ash content being the major concern to the washeries, the perfection in predicting the anticipated yield of clean coal is a pre-requisite step in treating a coal in an existing washery or in designing a new plant. At present recovery of clean coal from the washery rejects/middlings is the

major concern to maximise the utilisation of coking coal. It is required to recover the additional carbon values by beneficiating these tailings to reduce ash content. Simple conventional washing techniques are not effective to yield good quality clean coal from these tailings. Vigorous R & D efforts are needed in this direction for proper utilisation of Indian coking coal washery tailings for metallurgical industries, cement and chemical industries. Froth flotation is one of the established techniques to recover the additional clean coal from these tailings [4-5].

Froth flotation is a well established fine particle separation process based on the difference in surface hydrophobicity of different components. The selectivity of the separation is based on differences in particle surface properties. Separation of required solids is achieved when the surface properties of a valuable solid component are preferentially attached to the air bubbles. This can be achieved by using different types of flotation machines popularly known as flotation cells. In contrast to widely used flotation machines, which resemble continuous stirred reactors, there have been recent developments in flotation machines, which are similar to counter-current reactors popularly known as flotation columns [4-7].

Keeping this in view, the investigations were carried out on coking coal washery tailings generated by the flotation circuit of a coking coal washery in Eastern India for possibility of further beneficiation to recover the maximum clean coal. Beneficiation by both conventional cell and column flotation studies were carried out to examine the maximum possibility of reducing the ash content of the sample. An attempt has been made to evaluate the effects of different operating parameters on the flotation performance of both cell and column flotation. The results were compared to those from release analysis. This paper deals with some of the results obtained in this direction.

MATERIALS AND METHODS

Materials

Around 250 kg of flotation tailings generated at a coking coal washery in Eastern India was collected and used for this investigation. The whole sample was thoroughly mixed and a representative sample was drawn for wet size and chemical analysis by standard cone and quartering sampling method. The rest material was then wet screened at 500 micron sieve and the oversize material was ground in ball mill for short time to pass through the 500 micron sieve. Two representative samples from this -500 micron size coal fines were taken for size analysis and release analysis respectively. The rest material was used for flotation study. Commercial grade light diesel oil was used as the collector and MIBC (Methyl Iso-Butyl Carbinol) or commercial grade Nalco reagent was used as frother. Commercial sodium silicate was used as silica depressant as well as dispersant.

Methods

Size and chemical analysis

The standard BSS (British Standard System) sieves were used for wet size analysis of the as received sample as well as the -500 micron size coal fines. Each size fractions was then dried, weighed and sent for chemical (proximate) analysis. The chemical (proximate) analysis in moisture free basis was carried out by using LECO TGA-601 (Thermo-gravimetric analyzer) as per the ASTM standard procedure.

Release analysis

In order to determine the floatability of this coking coal tailings fines, the release analysis test developed by Dell was carried out [8]. These studies were carried out on below 500 μ size flotation feed material in standard laboratory Denver D-12 sub-aeration flotation cell using the standard

test procedure. The products were analyzed for ash in moisture free basis.

Cell flotation studies

Batch flotation tests were carried out using Denver D-12 sub-aeration flotation machine with 4 litre capacity cell. About 400 gm sample was taken in each experiment. The slurry of 40% solid concentration with water was prepared and whenever required, conditioned with required dosage of sodium silicate, for depression as well as dispersion of silica particles, for 5 minute at 1500 rpm. Further required amount of commercial grade light diesel oil was added as collector and conditioned for 5 min. The solids concentration was brought down to 10% by weight by adding additional water in the cell after which the required amount of MIBC (Methyl Iso-Butyl Carbinol) was added as frother and conditioned for one minute. After conditioning, the three stage cell flotation was carried out by releasing the air. Two stage cleaning of rougher concentrate was carried out without using any further reagent. The experiments were carried out at different operating parameters. Later on, the batch flotation study was conducted at the best conditions obtained, by using Nalco reagent as frother in place of MIBC. The batch flotation cleaner concentrate, rougher tailings and cleaner tailings were collected separately in each experiment and then dried, weighed and analyzed for ash in moisture free basis.

Column flotation studies

The column flotation studies were carried out by employing a 100 mm diameter laboratory glass column flotation set up. The schematic diagram of the experimental set up is shown in Fig. 1. Initially, 20 kg of coal sample was conditioned with the required dosage of sodium silicate at 40% solid concentration in the conditioner and then it was further conditioned with the required dosage of diesel oil as collector. Additional water was added to reduce the solid concentration from 40% to 10% in a 200 litre capacity conditioner. The compressed air was bubbled through the diffuser from a rotameter before adding water in the column to prevent the entry of water to the diffuser. The required volumetric flow rate of air was maintained and measured through rotameter. Initially, water and Nalco reagent as frother were pumped to column to generate air bubbles inside the column. Simultaneously wash water was added through peristaltic variable speed pump. Subsequently, the slurry was fed by peristaltic slurry pump at a specified rate to the column. The concentrate and tailings were collected, simultaneously for fixed interval of time, when the slurry flow rate of both feed and tailings became almost constant. Similarly, the cleaning of the rougher concentrate was carried out without adding any reagents. The two stage column flotation experiments were conducted at different operating parameters to optimise the process variables. All the concentrates and tailings samples collected in each experiment were then dried and weighed. For analysis of samples, similar procedure, as in case of the conventional cell, was followed.

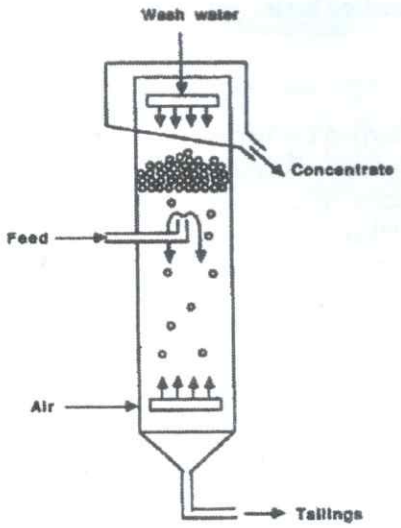

Fig. 1. Schematic diagram of flotation column

RESULTS AND DISCUSSION

Characterisation studies

The proximate analysis of the as received coking coal washery tailings are given in Table 1. The size and ash % of as received sample and as received sample ground to below 500 micron size are presented in Fig. 2 - 3 respectively. The results indicate that the ash percentage is unevenly distributed in all the size fractions. This clearly indicates that the present separation system is not effective for above 500 micron size coal. Hence, it is decided to reduce the +500 micron size fractions to below 500 micron size and mixed with the -500 micron size fractions to recover the additional clean coal.

Table 1
Proximate analysis of the coking coal fines

Details	Percentage, %
Moisture	0.7
Volatile matter	19.1
Ash	41.8
Fixed carbon	38.4

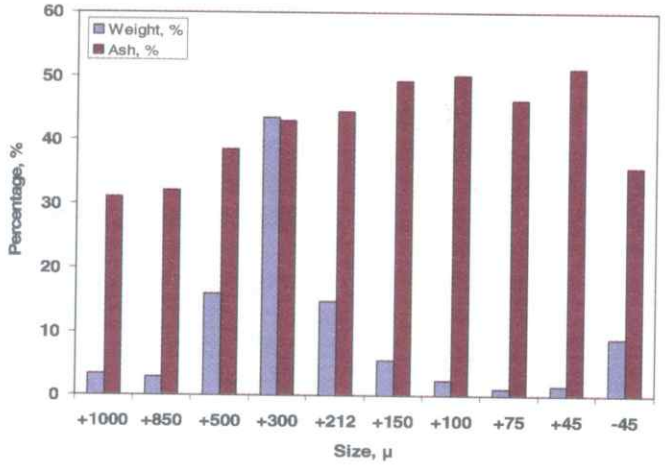

Fig. 2. Size and ash % of as received sample

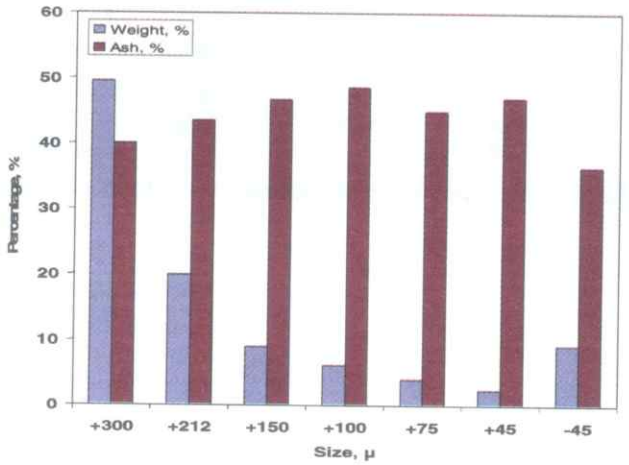

Fig. 3. Size and ash % of as received sample ground to below 500 micron size

The release analysis was conducted using the standard test procedure [8]. The test results are shown in Fig. 4. The results indicate that this tailings sample has potential to give a clean coal of 14.92% ash level at a yield of 22.08%.

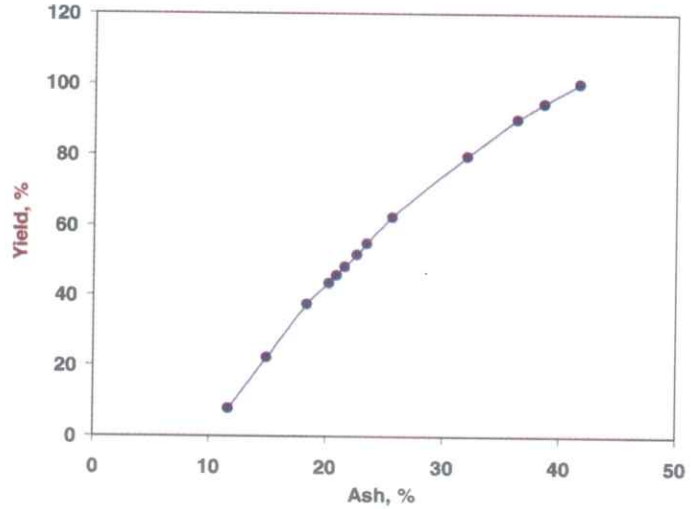

Fig. 4. Release analysis of tailings sample

Cell flotation studies

Initially three stage batch flotation studies were carried out using the conventional reagents like diesel oil and MIBC as collector and frother respectively. The effect of collector at different frother levels was studied and the results are depicted in Fig. 5 - 9.

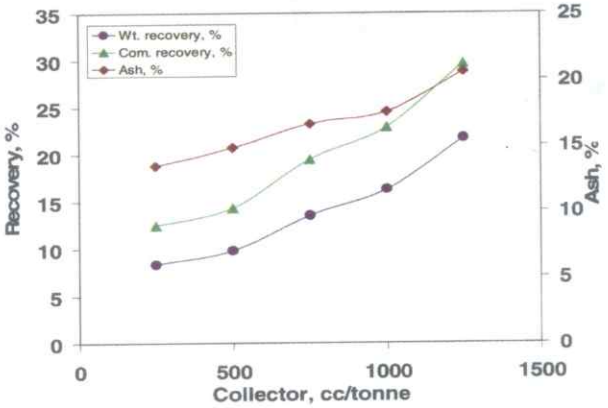

Fig. 5. Effect of collector at 50 cc/tonne of frother

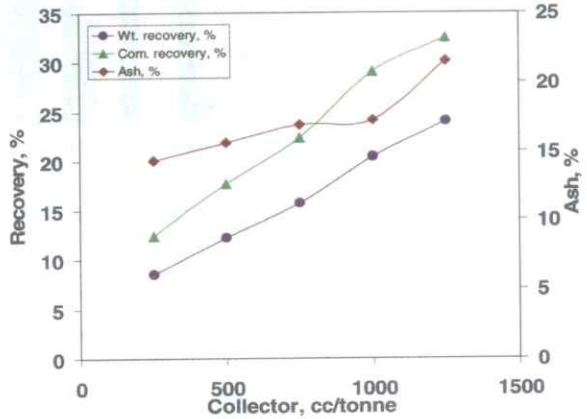

Fig. 6. Effect of collector at 100 cc/tonne of frother

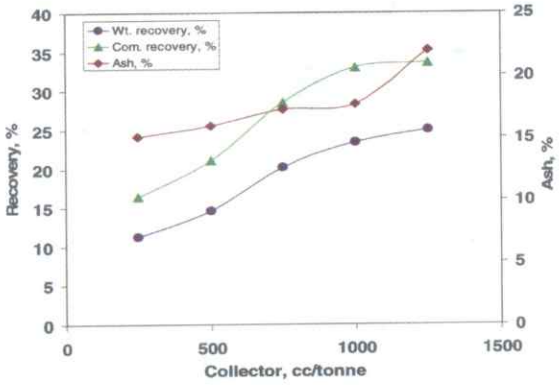

Fig. 7. Effect of collector at 150 cc/tonne of frother

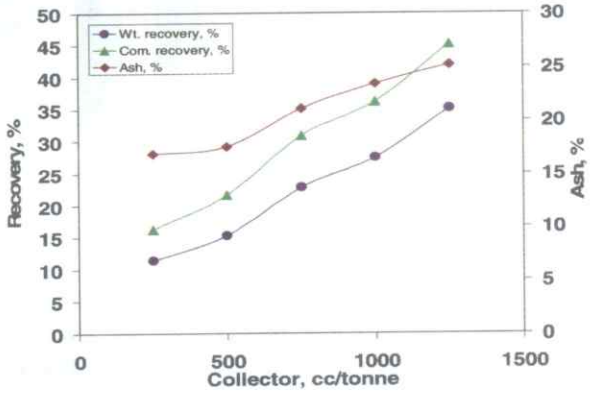

Fig. 8. Effect of collector at 200 cc/tonne of frother

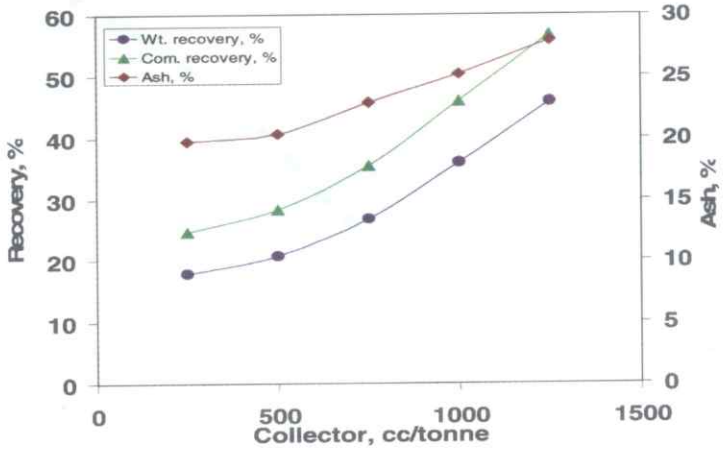

Fig. 9. Effect of collector at 250 cc/tonne of frother

Subsequently the effect of frother at different collector dosages was studied and the results are shown in Fig. 10 - 14. These results indicate that the flotation response was poor at lower dosage of collector hence the yield and combustible recovery were very low. It has been observed here that the yield increases with increase in collector concentration and so does the combustible recovery as well as the ash content of the clean coal. It has been reported by many investigators that the ash content of the flotation concentrate increases when recovery increases [9-14]. It indicates that higher dosage of collector and frother is required to enhance the floatability. It was observed that the yield of concentrate is not appreciable at the required ash level in the concentrate. From these studies, it has been observed that at the desired ash level of the concentrate, the recovery of clean coal is not appreciable, the rougher tailings is not rejectable/discardable tailings and the cleaner tailings is also not to the level of satisfaction. It has been found that 23.42% yield of the clean coal was obtained at 17.69% ash content with 32.99% combustible recovery at 1000 cc/tonne of collector and 150 cc/tonne of frother.

Further, experiments were conducted by adding sodium silicate as silica depressant prior to the collector at the best conditions obtained earlier. The results of the effect of depressant at the best dosages of collector and frother is shown in Fig. 15. The results indicate that better quality clean coal with acceptable ash content could be obtained. As the sodium silicate amount increases, the yield of the concentrate is decreased and so does the ash content of the clean coal as well as combustible recovery. It has been observed that with 2.00 kg/tonne of sodium silicate at 1000 cc/tonne of collector dosage and 150 cc/tonne of frother dosage, a clean coal with 14.23% ash can be achieved at an yield of 17.76% with 26.19% combustible recovery.

Further an attempt was made to recover the clean coal from the coking coal tailings at the best conditions obtained by using commercial Nalco reagent in place of MIBC in the batch flotation studies. The results of the effect of depressant with Nalco reagent are depicted in Fig. 16. It has been observed that with the same dosages of Nalco reagent as frother, the yield of cleaner concentrate is increased by 2% at almost same ash level. The rougher tailings contains 75.21% ash content with a yield of 32.87% can be discarded. The 1st and 2nd cleaner tailings at 33.56% and 13.84% yield with the ash content of 32.53% and 23.10% can be utilised for power generation and cement industries respectively.

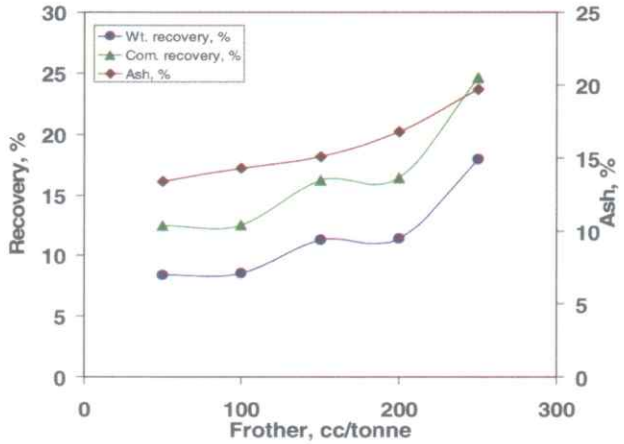

Fig. 10. Effect of frother at 250 cc/tonne of collector

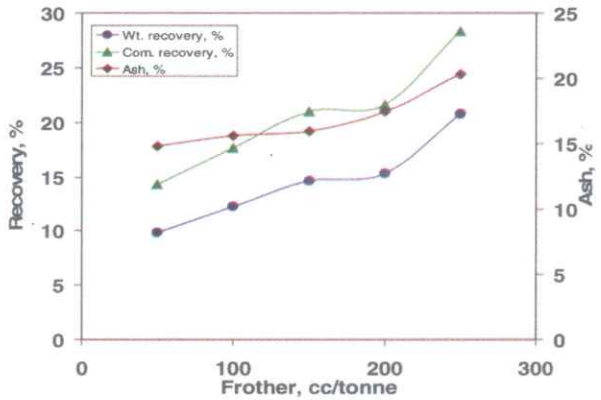

Fig. 11. Effect of frother at 500 cc/tonne of collector

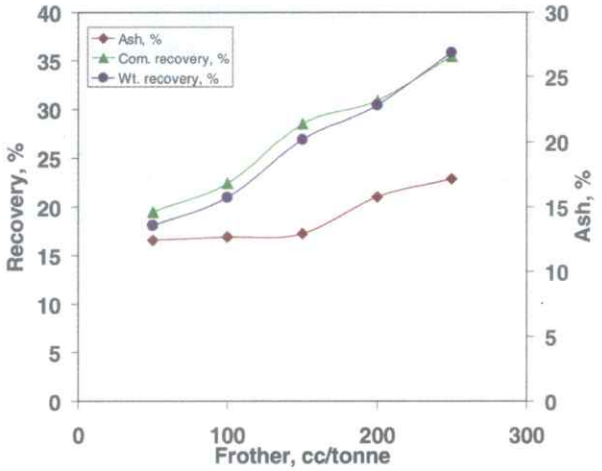

Fig. 12. Effect of frother at 750 cc/tonne of collector

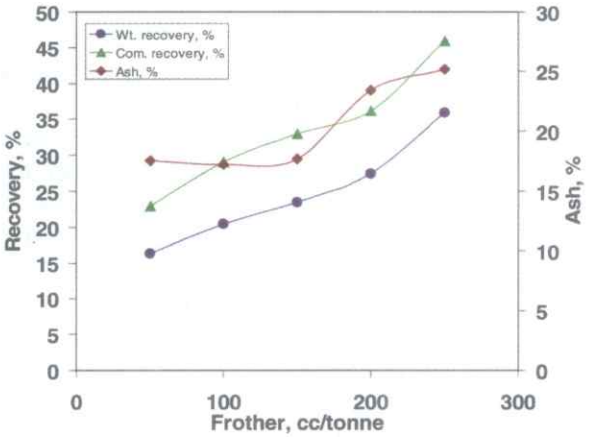

Fig. 13. Effect of frother at 1000 cc/tonne of collector

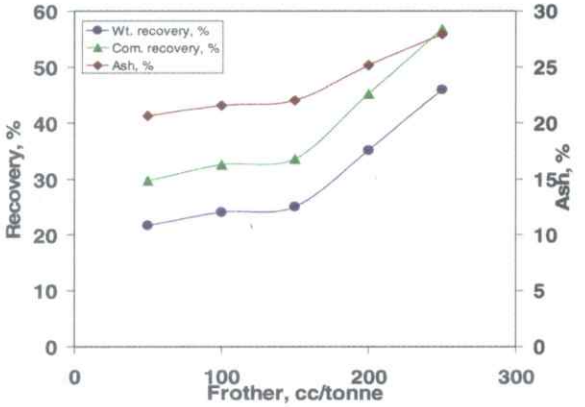

Fig. 14. Effect of frother at 1250 cc/tonne of collector

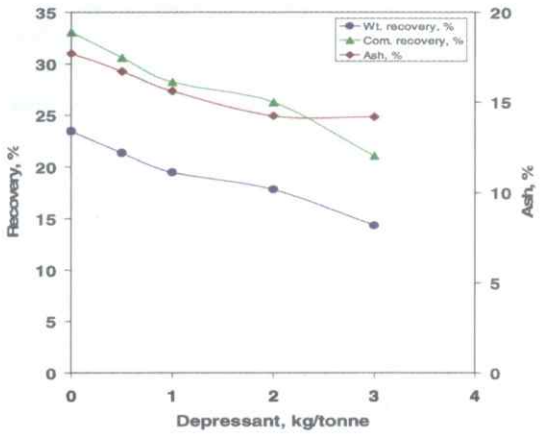

Fig. 15. Effect of depressant with MIBC as frother

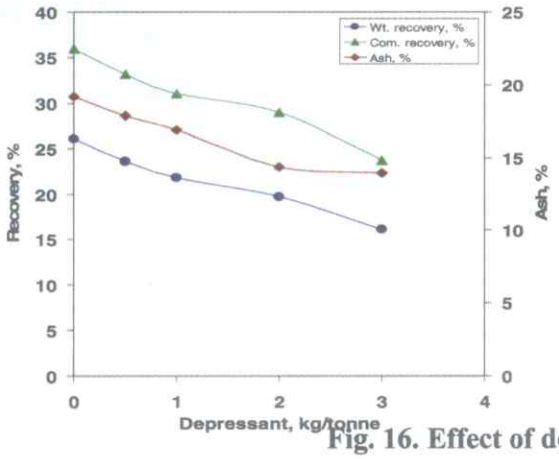

Fig. 16. Effect of depressant with Nalco reagent as frother

Column flotation studies

Two stage column flotation studies were carried out at 10% feed solids, 2.0 kg/tonne sodium silicate, 1000 cc/tonne light diesel oil and 150 cc/tonne Nalco reagent, which were found effective in earlier conventional batch flotation studies. The effects of column operating parameters like; air rate, wash water rate and feed rate were evaluated to achieve better performance during flotation. The effects of air rate at different operating conditions such as feed rate and wash water rate are shown in Fig. 17 - 19. As the air rate increased the clean coal yield and combustible recovery increased along with the ash content. This is due to mixing in the flotation zone, turbulence in the column axial direction and disturbance in froth bed [4, 12, 15-19]. At the lower feed rate, the performance of column flotation was better when compared to higher feed rates with respect to ash content of the clean coal. With the increase in feed rate, the number of gangue particles entrained in the cleaning zone increased leading to an increase in the ash content and also increase in the yield and combustible recovery. The ash content of clean coal decreased along with the combustible recovery and yield, with an increase in wash water. The gangue particles entrapped in the froth were removed with an increase in wash water rate, thereby decreasing the ash content of the clean coal [4, 20]. At 2.5 lit/min feed rate and also 2.5 lit/min wash water rate, when the air rate was maintained at 9.0 lit/min, the clean coal with 13.56% ash content at an yield of 21.03% with 31.13% combustible recovery as cleaner concentrate by two stage column flotation was obtained. Further increase in air rate caused significant increase in the yield and combustible recovery simultaneously the clean coal ash content also increased significantly. The air rate has got significant effect compared to wash water rate and feed rate [20-23].

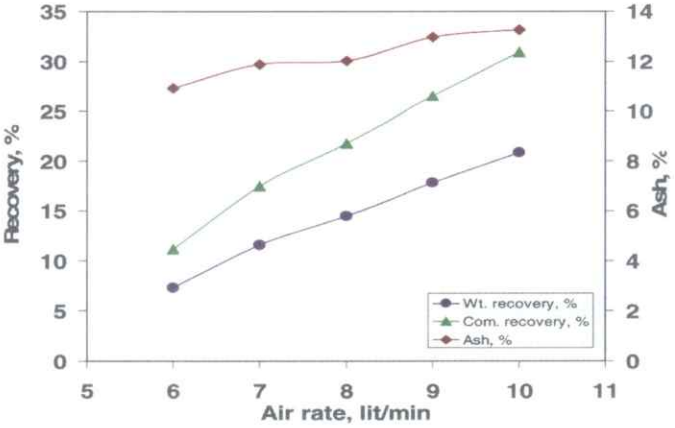

Fig. 17. Effect of air rate in column flotation

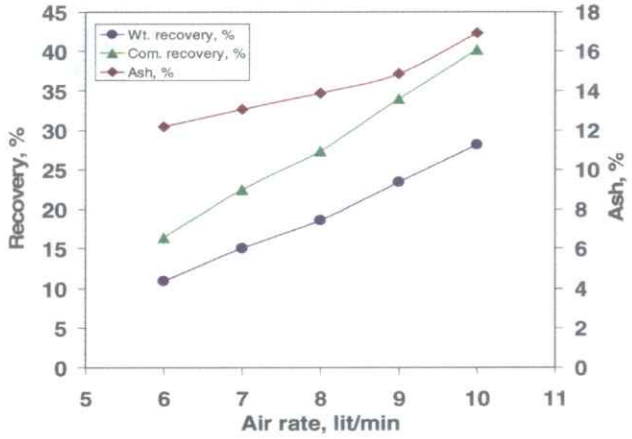

Fig. 18. Effect of air rate in column flotation

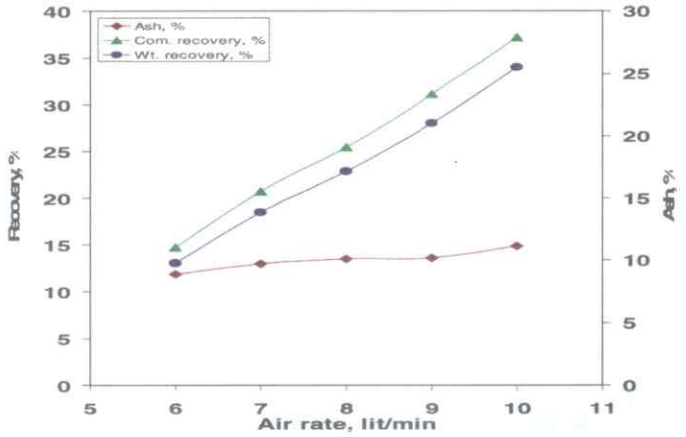

Fig. 19. Effect of air rate in column flotation

Comparison of flotation performance

Release analysis indicated that the sample has potential to give a clean coal of 14.92% ash content at a yield of 22.08%. The conventional cell flotation was able to produce a clean coal of 19.73% yield with 28.97% combustible recovery at an ash content of 14.34%. Using column flotation, a clean coal with an ash content of 13.56% at a yield of 21.03% with 31.13% combustible recovery can be obtained at the same regent dosages and solids concentration. The performance of both conventional and column flotation is compared with respect to release analysis and shown in Fig. 20. It is clear from the figure that the performance of column flotation is close to release analysis and can produce better clean coal in terms of lower ash content [20, 24-26]. Also some conventional flotation results are close to release analysis at very high ash content of the clean coal. At this level of ash content, both conventional and column flotation are showing almost similar performance.

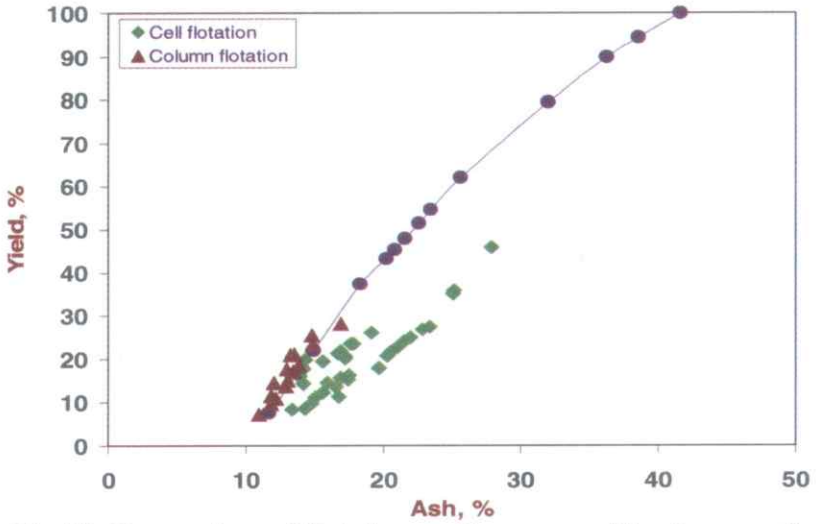

Fig. 20. Comparison of flotation performance with release analysis

CONCLUSION

The flotation studies carried out on the coking coal washery tailings reveal that the material responds well to flotation to recover additional clean coal. The three stage flotation in a conventional cell reduced the ash content from 41.8% to 14.34% at a yield of 19.73% with 28.97% combustible recovery. Nalco regent in place of MIBC as frother has given better performance in flotation. Using, two stage column flotation, the ash content of the clean coal was further reduced to 13.56% at 21.03% yield with 31.13% combustible recovery. The tailing generated during the study are low in carbon content and rejectable tailings. Simultaneously, the cleaner tailings generated can be utilised directly either for cement industries or thermal power generation. The present study reveals that the column flotation is more efficient in comparison to the conventional cell. The results of column flotation are close to that of release analysis.

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REFERENCES

[1]. M. S. Jena, S. K. Biswal, S. P. Das and P. S. R. Reddy, Beneficiation of coking coal fines by flotation, Proceedings of the International Seminar on Mineral Processing Technology [MPT – 2007], Mumbai, (2007) pp.193-196.

[2]. V. N. Misra, P. S. R. Reddy and S. K. Biswal, Beneficiation of non-coking coal for metallurgical purposes, CCAI Monthly New Letter May, (2003) pp. 27-36.

[3]. S. K. Biswal, M. S. Jena, A. K. Sahoo and P. S. R. Reddy, Study on the performance of mineral jig for beneficiation of fine non–coking coal, Proceedings of the International Conference on Emerging Trends in Mineral Processing and Extractive Metallurgy [ICME – 2005], Bhubaneswar, (2005) pp. 126-132.

[4]. M. S. Jena, S. K. Biswal, S. P. Das and P. S. R. Reddy, Comparative study of the performance of conventional and column flotation when treating coking coal fines, Fuel Processing Technology, Vol. 89, (2008) pp. 1409-1415.

[5]. M. S. Jena, S. K. Biswal and M. V. Rudramuniyappa, Study on flotation characteristics of oxidised Indian high ash sub-bituminous coal, International Journal of Mineral Processing, Vol. 87, (2008) pp. 42–50.

[6]. D. A. Wheeler, 'Big flotation column mill tested', Engineering and Mining Journal, Vol. 167, (1966) pp. 98–100.

[7]. S. Sastri, P. S. R. Reddy, K. K. Bhattacharyya, S. G. Kumar and K. S. Narasimhan, Recovery of coal fines using column flotation, Minerals Engineering, Vol. 1, (1988) pp. 359–363.

[8]. C. C. Dell, An Improved Release Analysis Procedure for Determining Coal Washability, J. Inst. Fuel, 37 (1964), pp. 149 – 150.

[9]. F. F. Aplan, Coal Flotation, in : A. M. Gaudin Memorial Volume, M. C. Fuerstenuau (Ed.), Published by American Institute of Mining, Metallurgical and Petroleum Engineers, Inc. New York, Chapter 45, 2 (1976), pp. 1235 – 1264.

[10]. G. Ozbayoglu, Coal Flotation, Mineral Processing Design, B. Yarar and Z. M. Dogan (Eds.), Series E: Applied Sciences No. 122 (1967), pp. 76-04.

[11]. S. K. Biswal, P. S. R. Reddy, S. Prakash, S. K. Bhaumik, S. R. S. Sastri, Flotation Column - A Novel Technique for Fine Coal Beneficiation, Mintech, 21 (2000), pp. 26-33.

[12]. S. K. Biswal, Studies on Flotation Cell and Modelling of Flotation Column for Beneficiation of Indian High Ash Oxidised Non-Coking Coal, Ph. D. Thesis, IIT, Kharagpur, (2001).

[13]. S. K. Nicol, J. B. Smitham, J. T. Hinkley, Measurement of Coal Floatation Efficiency using the True Floatation Technique, In W. S. Blaschke (Ed.) Proc. 12th Int. Coal Preparation Congress (Cracow, May 1994), Gordon and Breach, New York, (1996), pp. 741-746.

[14]. M. S. Jena, S. K. Biswal, K. K. Rao and P.S. R. Reddy, Studies on coal flotation in flotation column using statistical technique', Int. J. Oil, Gas and Coal Technology, Vol. 2, No. 1, 2009, 2009, pp. 58-69.

[15]. J. A. Finch, G. S. Dobby, Column Flotation, Pergamon Press, Oxford, U.S.A. (1990).

[16]. J. G. Groopo, B. K. Parekh, Continuous Pilot Scale Testing of Column Flotation for Recovery of Fine Coal, Mining Engineering, 42 (1990), pp. 1189 – 1192.

[17]. P. Mavros, K. A. Kydros, K. A. Matis, Arsenopyrite Enrichment by Column Flotation, Minerals Engineering., 6 (1993), pp. 1265 – 1277.

[18]. D. Tao, G. H. Luttrell, R. H. Yoon, A Parametric Study of Froth Stability and Its Effect on Column Flotation of Fine Particles, International Journal of Mineral Processing, 59 (2000), pp. 25 – 43.

[19]. C. M. Goodall, C. T. O'Connor, Residence Time Distribution Studies in a Flotation Column, Part 2: The

Relationship between Solids Residence Time Distribution and Metallurgical Performance, International Journal of Mineral Processing, 36 (1992), pp. 219 – 228.

[20]. P. S. R. Reddy, S. Prakash, K. K. Bhattacharyya, S. R. S. Sastri, K. S. Narasimhan, Flotation Column for the Recovery of Coal Fines, K. V. S. Sastry (Ed.), Column Flotation'88, Proceedings of an International Symposium on Column Flotation, SME, Phoenix, (1988), pp. 221 – 226.

[21]. R. Laplante, J. M. Toguri, H. W. Smith, The effect of air flow rate on the kinetics of flotation: Part 1. The transfer of material from the slurry to the froth, International Journal of Mineral Processing, 11 (1983a), pp. 203 – 219.

[22]. R. Laplante, J. M. Toguri, H. W. Smith, The effect of air flow rate on the kinetics of flotation: Part 2. The transfer of material from the froth over the cell lip, International Journal of Mineral Processing, 11 (1983b), pp. 221 – 234.

[23]. R. H. Yoon, G. H. Luttrell, G. T. Adel, M. J. Mankosa, Recent advances in fine coal flotation, In: S. Chander, R. Klimpel (Eds.), Advances in Coal and Mineral Processing Using Flotation, SME, Littleton, (1989), pp. 211 – 218.

[24]. P. R. Forrest, Processing of high sulfur coals using microbubble column flotation, Thesis, Department of Mining and Minerals Engineering, Virginia Polytechnic Institute and State University, Blacksburgh, (1990).

[25]. K. N. Subramanian, D. E. G. Lonnelly, K. Y. Wong, Commercialization of a column flotation circuit for gold sulphide ore, K. V. S. Sastry (Ed.), Column Flotation'88, Proceedings of an International Symposium on Column Flotation, SME, Phoenix, (1988), pp. 13 – 18.

[26]. D. Tao, G. H. Luttrell, R. H. Yoon, An experimental investigation on column flotation circuit configuration, Int. Journal of Mineral Processing, 60 (2000), pp. 37-56.

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BENEFICIATION OF LOW-GRADE IRON ORE BY FLOTATION

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ABSTRACT

In the present work an effort has been made to study the beneficiation of low grade iron ore fines by flotation process. For this purpose the samples were obtained from B.B.H Mines, Chitradurga, Karnataka. The samples were initially subjected for mineralogical studies. The microscopic analyses showed that the sample contains 28% hematite, 33% goethite, 15% limonite, 4% magnetite and 20% gangue. Form and habit of hematite and magnetite was found to be sub-hedral and anhedral respectively. After conducting microscopic studies the ore was subjected for chemical analyses. The results of chemical analyses showed that the ore contains 47.02% Fe. After completion of the characterisation studies the samples were subjected for comminution to produce 80% passing 75 micron size fractions. Further flotation tests are being envisaged using dodecyl amine as the collector, MIBC as the frother and sodium silicate as the depressant. From the results obtained from the flotation process it was possible to recover 45.2% iron with the concentrate grade of 59.2%.

INTRODUCTION

Iron is the second most abundant metallic element in the earth's crust & accounts for 5.6% of the lithosphere. The principal minerals of iron are the oxides (hematite & magnetite), hydroxides (limonite & goethite), carbonate (siderite) & sulphide (pyrite). Iron is the basic raw material for iron and steel industry. India is an important producer of iron ore in the world contributing more than 7% of the production (Detailed dossier on iron ore in India, Indian Bureau of Mines, 2005). Orissa, Chattisgarh, Karnataka, Jharkhand and Goa are the major iron ore producing states in India. The beneficiation of iron ore is done by the methods such as gravity concentration, magnetic separation, flotation and flocculation. Most beneficiation operations result in three products: a concentrate, a middling (which is either reprocessed or stock piled) and a tailing (waste). The early mining activities were focussed on high grade deposits that did not require complicated beneficiation. Following the increase in consumption, with consequent depletion of these deposits, it became necessary to deploy improved techniques to enhance the recovery, leading to more sensible use of ore reserves. Increasing demand for the production of steel worldwide and advanced steel making techniques have necessitated the use of low grade as well as finely disseminated iron ores. From the past decade it is observed that there is a phenomenal increase in the production of iron ore in India. Apart from the production of high-grade ores, many industries are exploring the possibility of beneficiation of low-grade ores for the production of iron and steel. From the literature (Rocha et al. 2010), it may be seen that flotation of low grade iron ore fines has been carried out effectively. The role of different reagents used in flotation was studied. It was found that the flotation should be performed at pH as low as possible. This helps to reduce the consumption of caustic soda (Araujo et al 2004). It is seen that humic acid can be used as an alternative depressant (Santos et al, 2007). It was found that after conditioning with humic acid at pH 10.2, low dodecylamine concentrations, the contact angle presented by hematite was much less than that presented by quartz. An increase in Fe content is observed when a particular type of sodium silicate with proper dosage is used (Rao et al, 2011). They found that the concentrate of 58.89 wt % Fe can be obtained from iron ore slimes with 54.44 wt % Fe, when sodium silicate with a soda to silica mole ratio of 2.19 is used as a depressant at a feed rate of 0.2kg/ton. Panda et al, (2010) suggested that the product recovery and grade was affected more by the pH of slurry and the solid concentration as compared to the dosage of flocculants. A literature review on gravity concentration

(Singh et al, NML Laboratory, Jamshedpur) suggested that the problem with gravity concentration processes is that it is less effective in treating particles in relatively finer size range because the viscous forces are more dominant as compared to gravity forces in finer size range. This affects the separation efficiency. So the beneficiation of low grade metallic and non-metallic ores can be done more efficiently by the combination of gravity and flotation or magnetic separation. Apart from beneficiation, flotation is also being utilized in the recent years for the up gradation of slimes generated in the iron ore processing plants. An attempt has been made to study the beneficiation of low grade iron ores using different dosages of reagents such as dodecylamine (collector), MIBC (frother) and sodium silicate (depressant).

MATERIALS AND METHODS

Material

The iron ore sample used in the study was obtained from B.B.H Mines, Chitradurga, Karnataka. The representative sample was subjected to mineralogical analysis. The microscopic analyses showed that the sample contains 28% hematite, 33% goethite, 15% limonite, 4% magnetite and 20% gangue. The sample was subjected to comminution to produce 80% passing 75 micron size fractions. After conducting microscopic studies the ore was subjected for chemical analyses. The results of chemical analyses showed that the ore contains 47.02% Fe.

Reagents

For conducting flotation experiments, the reagents used are dodecyl amine as collector, MIBC as frother and sodium silicate as depressant. Sodium hydroxide (NaOH) was used to get the required pH.

Flotation Tests

The flotation tests were carried out in a 3000ml capacity flotation cell. During the studies desired amount of mineral (20% pulp density by wt.) was mixed with 250 ml of water and the required pH (pH 9) of the slurry was adjusted using dilute NaOH. The slurry was allowed to condition for 10 minutes. Sodium silicate (depressant) was added and conditioned for 2 minutes. Dodecyl amine (collector) was added and conditioned for 2 minutes. A few drops of MIBC (frother) were added and conditioned for 1 minute. The suction valve was opened and the machine was run to collect the froth for 30 sec, 60 sec, 90 sec, 120 sec and 150 sec. The froth was allowed to dry and weighed. The chemical analysis of the dried samples was performed. The tailings were also kept for chemical analysis. The recovery, grade and flotation constant were calculated using the mass balance equations.

RESULTS AND DISCUSSION

After completion of mineralogical studies, the representative sample was subjected to comminution to produce 80% passing 75 micron size fraction. Some tests were carried out with the required amount of material (469 grams) at 20% pulp density by weight. The pH of the slurry was maintained at 9 by using NaOH. First experiment was performed with the collector dosage of 0.75kg/ton, frother dosage of 0.5kg/ton and depressant dosage of 0.025kg/ton. The results obtained are given below in Fig. 1.

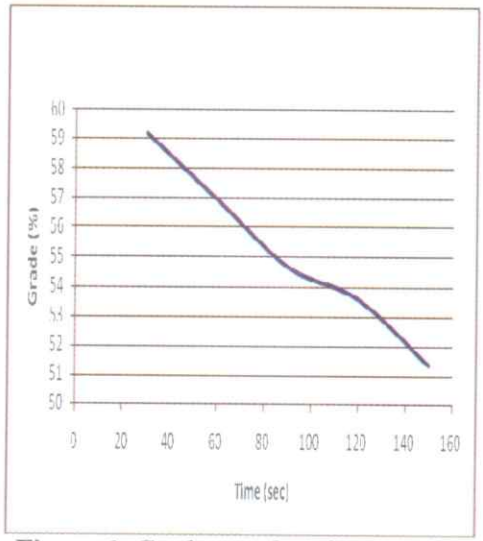

Figure 1. Grade as a function of time.

When the grade was plotted as a function of time (figure 1), it was found that the grade goes on decreasing with time. The maximum grade of 59.2 was obtained in the first 30 seconds and this value went on decreasing with time. From the figure 2 it is seen that the recovery goes on increasing with time. The overall recovery of iron was found to be approximately 45% in 150 seconds. It can be seen that all the valuables float within a few minutes while it takes longer time for residual small quantity to float.

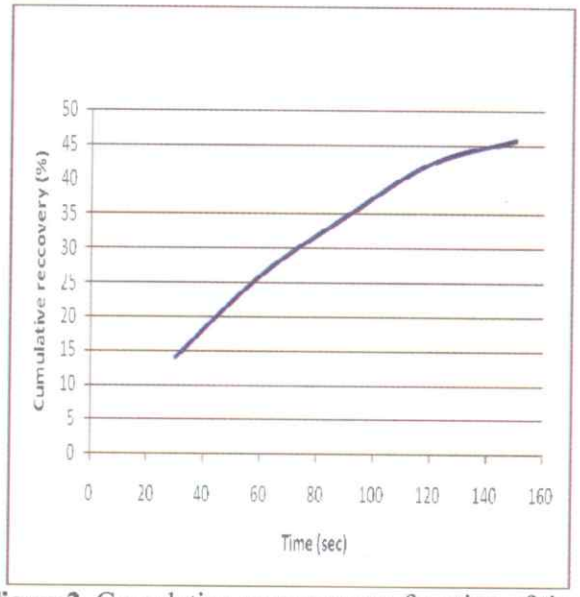

Figure2. Cumulative recovery as a function of time

Another graph was plotted with cumulative recovery as a function of grade which is shown in figure 3. The cumulative recovery decreases as the grade increases. The maximum recovery of 45.2% is obtained with a grade of about 51% where as the maximum grade of 59.2% is obtained with a recovery of about 14%.

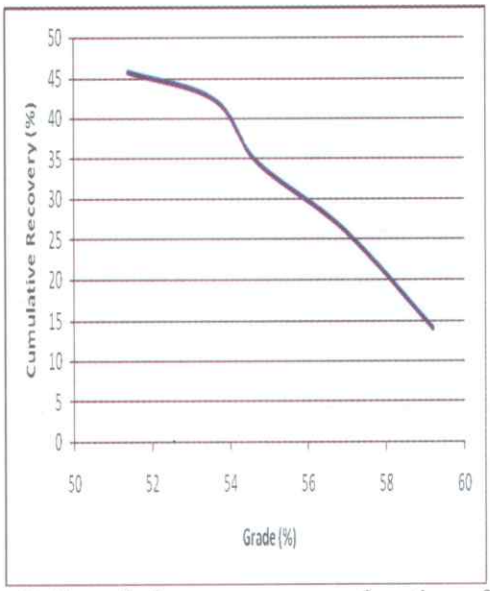

Figure 3. Cumulative recovery as a function of grade

Few more tests were carried out with the different sets of reagent dosages so as to increase the recovery up to 51% or more. Figure 4 was plotted between the natural log values of cumulative recovery and time. This curve was plotted to calculate the flotation rate constant (k). The curve was found to be straight line and the slope of this curve is called k. This shows that the flotation followed the first order kinetics. Theoretically it can be calculated from the equation given by Lynch (1985). The equation is given below:

$$R = 1\text{-}\exp(-kt)$$

Where R= cumulative recovery after time t.
t= cumulative flotation time in minutes

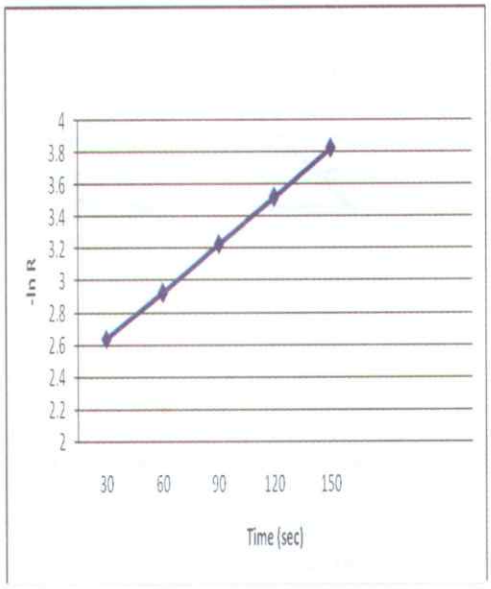

Figure 4. lograthmic value of cummulative recovery as a function of time

CONCLUSION

From the studies carried out on beneficiation of low grade iron ore, the following conclusions are drawn:

1. Iron ore samples received were pocessed of complex mineralogical nature containing 20% hematite, 35% goethite, 20% limonite, 5% magnetite and 20% gangue.

2. The flotation test indicated the maximum recovery of 45.2% with iron grade 59.2% as a concentrate using 20% pulp density with collector dosage of 0.75kg/ton, frother dosage of 0.5kg/ton and depressant dosage of 0.025kg/ton.

3. The kinetics studies carried out indicated that the flotation process follows well known first order kinetics rate constant of 0.593 which is in agreement with calculated value.

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Authors are thankful to B.B.H Mines, Chitradurga, Karnataka for supplying necessary samples.

REFERENCES

Araujo, A C, Viana P R M, Peres, A E C 2005. Reagents in iron ore flotation Minerals Engineering 18: 219–224.

Detailed information dossier on iron ore in India (2005), Indian Bureau of Mines. Chapter 1.

D. S. Rao, T. V. Vijaya Kumar, S S Rao, S Prabhakar and G Bhaskar Raju 2011. Effectiveness of sodium silicate as gangue depressants in iron ore slimes flotation, International Journal of Minerals, Metallurgy and Materials, Volume 18, Number 5, Page 515

I. D. Santos and J.'F. Oliveira 2007. Utilization of humic acid as a depressant for hematite in the reverse flotation of iron ore, Journal of Minerals Engineering, 20: 1003–1007.

Panda, L, Biswal, S K and Tathavadkar, V, 2010. Beneficiation of iron ore kaolinite mixtures using selective flocculation, Journal of Minerals and Material Characterization and Engineering, 9 (11):973-983.

Rocha, L, Caneado, R Z L and Peres, A E C, 2010. Iron ore flotation, Minerals Engineering, 23 (11-13):842-845.

Singh, R, Bhattacharya, K K and Maulik, S C, Gravity concentration of fines and ultra fines, National Metallurgical Lab: 40-56.

Wills, B A, 1985. Mineral Processing Technology, pp546-549 (Pergamon Press: Oxford).

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FLOTATION OF LIMESTONE REJECTS FOR VALUE ADDITION

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ABSTRACT

Investigations were carried out to beneficiate the lime stone rejects generated at a lime stone washing plant in southern India. This reject contains around 12.09% CaO, 2.95% MgO, 10.73% Al_2O_3 and 43.05% SiO_2. Characterisation studies revealed that the liberation of particles (calcite from gangue/ quartz) is maximum in the size range of 100 micron. Hence, Froth flotation process was adopted for its upgradation. Oleic acid and MIBC were used as collector and frother respectively. Sodium silicate was used as dispersant for siliceous minerals, sodium hydroxide and hydrochloric acid were used as pH regulator. By two stage flotation at 7.5 pH, considerable amount of silica and other gangue minerals were removed and CaO was upgraded to 42.5% with a yield of around 16.0%.

Keywords: Lime stone reject; froth flotation; concentrate; cement industry

INTRODUCTION

Limestone is a very essential raw material for the metallurgical industry as flux and in the manufacture of cement. It is one of the basic raw materials of industry and construction. Limestone is a sedimentary rock formed by the accumulation of sediments composed mainly of calcium or magnesium carbonate. It is compared with one leg of a six legged stool upon which modern industry rests, the other legs being coal, oil, iron ore, sulfur and salt. The major constituent of limestone is calcium carbonate. It is used in sugar, textile, glass and paper industries. Also it is used in blast furnace and steel melting process as a flux. In India more than 60% of limestone is used in cement industry. Day by day the high grade limestone resources are depleting and hence many of the industries are looking for utilization of the existing low grade limestone from their captive mines with proper beneficiation to meet the specification and demand. The low grade limestone cannot be used directly for cement making due to its poor quality. Beneficiation aims at improving the limestone quality so as to produce an economically usable raw material. The selection of beneficiation process depends upon mineralogy, physical and chemical characters of limestone. The beneficiation of limestone can be done by simple comminution (crushing & grinding), cleaning & classification. Gravity concentration process like jigging, tabling can be adopted if there is a considerable specific gravity difference between the desired and undesired minerals [1]. But due to negligible difference in the specific gravity of constituent minerals (calcite, quartz & clay), the gravity separation method cannot be applied with great success. Hence flotation was tried as it is one of most important and versatile mineral processing technique for fine particle processing and upgrading ore [2]. The main objective of the present work is to increase the grade of limestone with appropriate weight recovery. The experimental studies include the optimization of process parameters and generation of data required for scale-up.

EXPERIMENTAL

Materials

The -1 mm size generated from a limestone washing plant in southern India considered as reject was collected & used for the present investigation. Size of the collected sample was reduced to below 100 micron by ball mill. This below 100 micron size sample was taken for

flotation studies. During flotation experiments, oleic acid and commercial grade of sodium oleate were used as the collector (in the range of 100 - 500 cc/tonne and 0.5-2.5 kg/tonne, respectively) and MIBC as frother (in the range of 0 - 100 cc/tonne). Commercial grade sodium silicate was used as silica depressant (in the range of 1 - 5 kg/tonne). Hydrochloric acid and sodium hydroxide were used as pH regulators.

Method

A representative sample of around 100 kg prepared from the bulk reject sample after thorough mixing, was taken for wet size analysis. The standard BSS (British Standard System) sieves were used for wet size analysis. Two stage conventional cell flotation studies were carried out to evaluate the effects of different parameters and also for reagent optimisation.

Some preliminary flotation experiments were conducted to assess the stages of cleaning required for flotation studies as well as to evaluate the range of collector, frother and depressant dosage and also to know the range of pH. Response is measured in terms of weight % of corresponding concentrate and tailings. Grade in terms of CaO% for both concentrate and tailings was evaluated by wet chemical analysis. About 200 gm of sample were taken in each experiment and tests were carried out in a 2 lit. capacity cell. The slurry was prepared at 40% solid concentration with water and conditioned with required dosage of commercial grade sodium silicate for 5 minute at 1500 rpm. The pH was maintained at 7.5. Then required dosage of oleic acid or sodium oleate was added as collector and conditioned for 5 minute. The solids concentration was brought down to 10% by adding additional water. Subsequently, required dosage of MIBC was added as frother and conditioned for 1 min. Then two stage cell flotation was carried out using the induced air. The cleaning of rougher concentrate was carried out without using any further reagent. The cleaner concentrate, cleaner tailings and rougher tailings were then collected, dried and sent for chemical analysis.

RESULT AND DISCUSSION

Size and Chemical Analysis

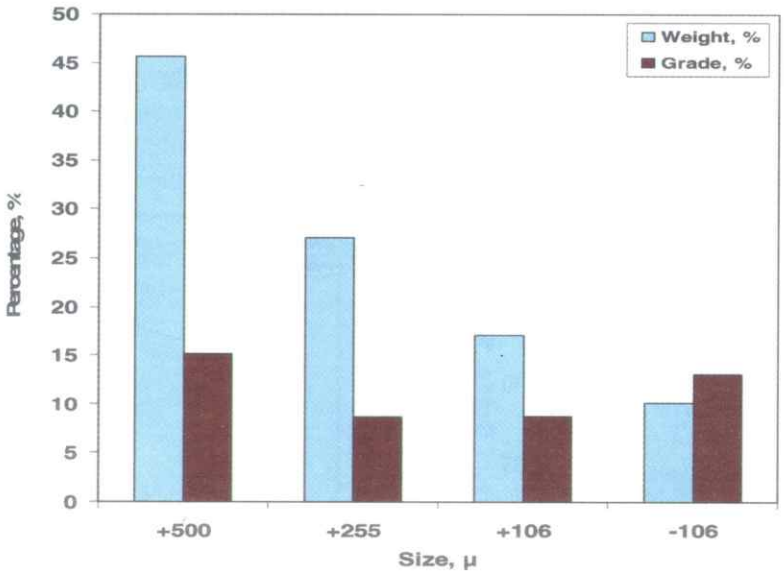

Fig.1 Size analysis of as received reject sample

The size and chemical analysis of 'as received' reject sample are shown in Fig. 1. The chemical analysis data indicate that the as received reject sample contains 12.09% CaO, 2.93% MgO, 10.73 % Al_2O_3, and 43.05 % SiO_2. The size and chemical analysis of as received sample indicate that the lime content is unevenly distributed in all the size fractions. Hence separation by classification is not possible. Froth flotation is the alternative separation process, which can be adopted for this type of fine particle processing. So, it was decided to grind the sample to below 100μ and the -100μ size sample was taken as the feed material for flotation studies [2]. The size and chemical analysis of the flotation feed material is shown in Fig. 2. The results indicate that the weight recovery is more in finer sizes, while the grade is reverse. Particularly in -45μ size fraction the weight recovery is too high.

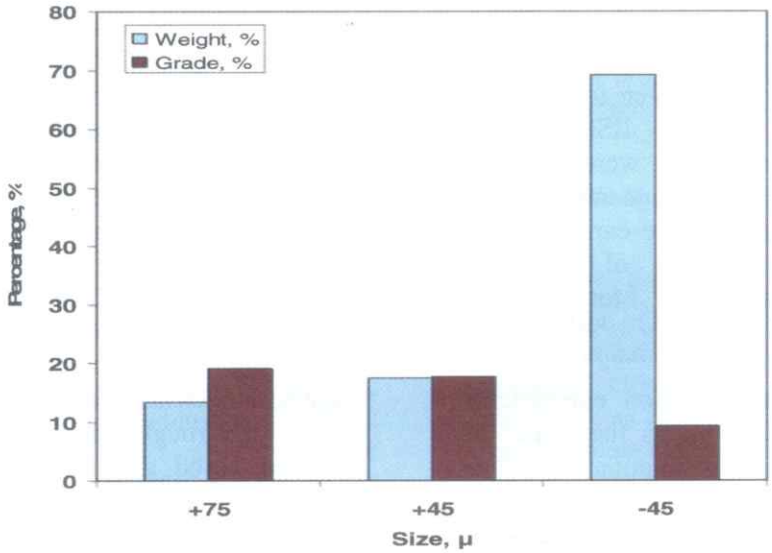

Fig. 2. Size and chemical analysis of as received sample ground to below 100 μ

Flotation Studies

The two stage conventional flotation experiments were conducted using Denver sub aeration flotation machine by varying different reagent conditions such as, depressant, collector and frother concentrations. The experiments were carried out by varying one variable at time and keeping all other parameters constant.

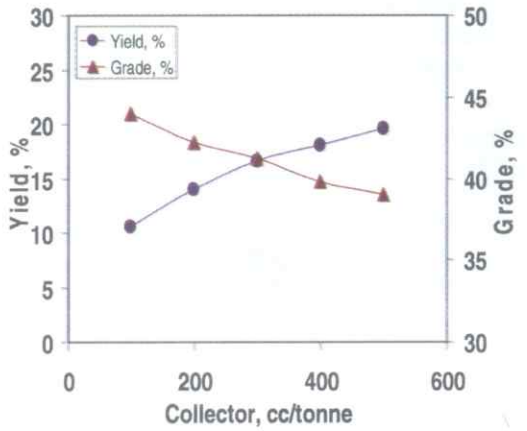

Fig. 3. Effect of collector without frother

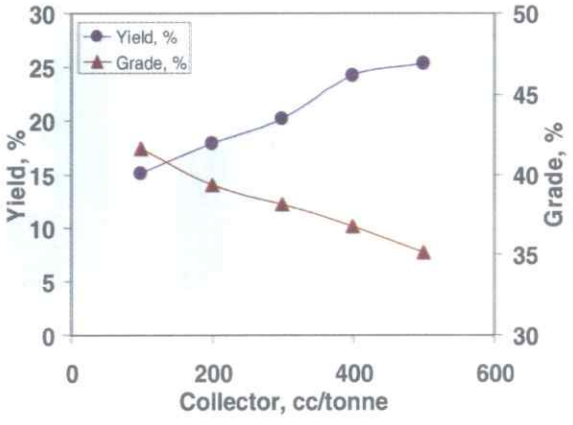

Fig. 4. Effect of collector at 25 cc/tonne frother

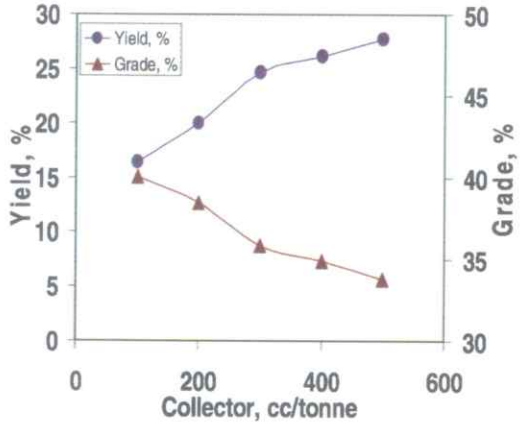

Fig. 5. Effect of collector at 50 cc/ tonne frother

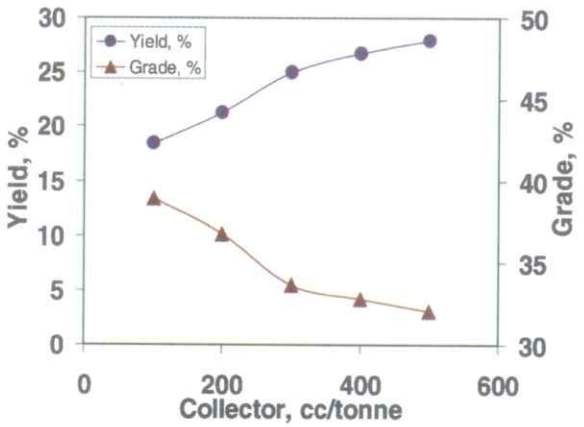

Fig. 6. Effect of collector at 75 cc/ tonne frother.

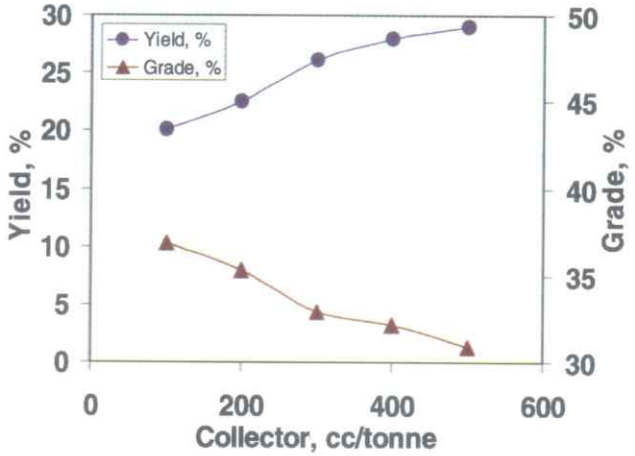

Fig. 7. Effect of collector at 100 cc/tonne collector

The effect of collector at different frother levels was studied and shown in Fig. 3 - 7. The results indicate that the flotation response is poor at lower dosage of collector; hence the yield is too low. The yield and grade show inverse relationship. At 300cc/tonne collector (oleic acid), a cleaner concentrate of around 41% is achieved with 17% yield at 2 kg/ton sodium silicate as silica depressant. Again, two stage cell flotation experiments are conducted using sodium oleate as collector in place of oleic acid and the results are depicted in Fig. 8.

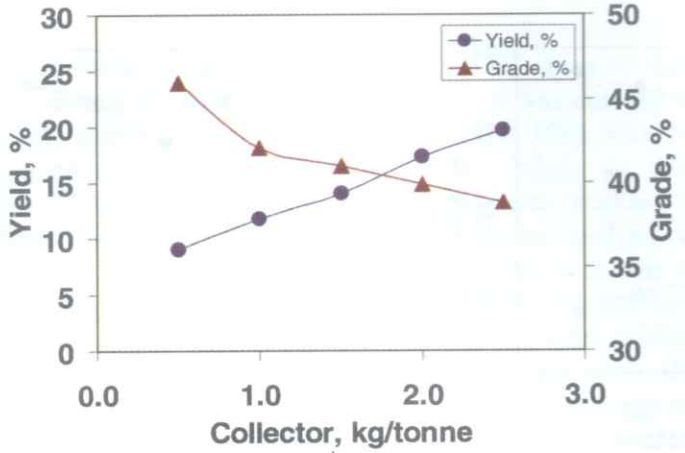

Fig. 8. Effect of sodium oleate as collector

The results indicate that a cleaner concentrate of around 39.88% CaO can be achieved with 17.29% yield at 2.0 kg/tonne of sodium oleate as collector and 2.0 kg/tonne of sodium silicate as depressant. It has been observed that the yield increases with increase in collector concentration but the grade decreases simultaneously.

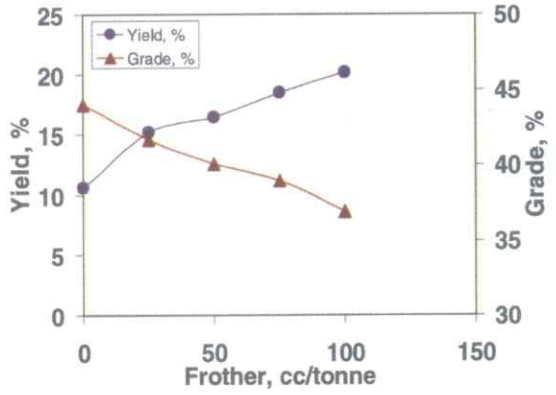

Fig. 9. Effect of frother at 100 cc/tonne collector

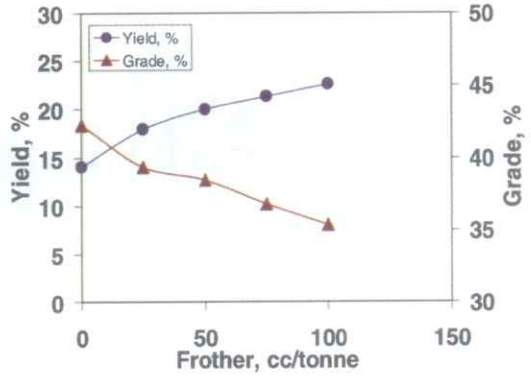

Fig. 10. Effect of frother at 200 cc/ tonne collector.

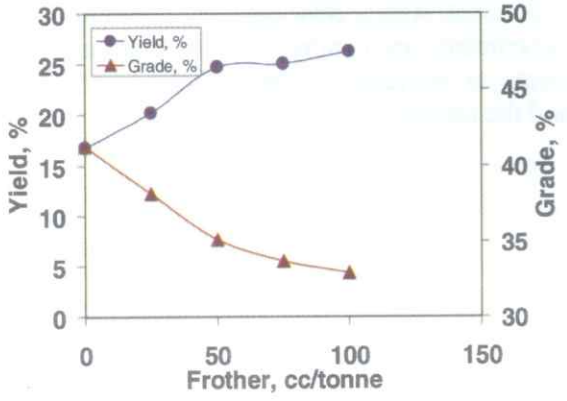

Fig. 11. Effect frother at 300 cc/tonne collector

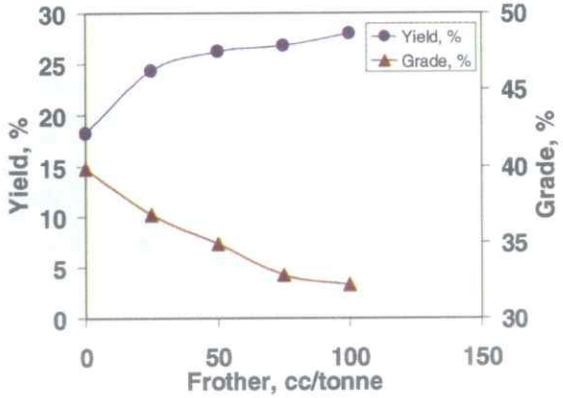

Fig. 12. Effect of frother at 400 cc/tonne collector.

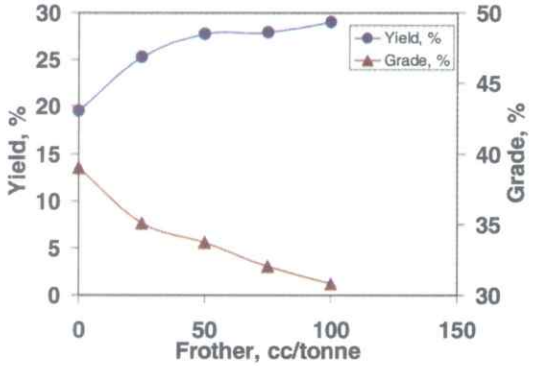

Fig. 13. Effect of frother at 500 cc/ tonne collector.

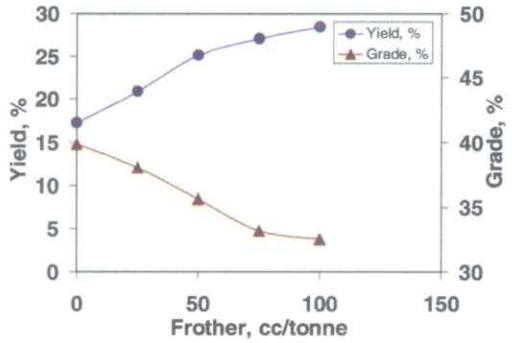

Fig. 14. Effect of frother with sodium oleate as collector

The effect of frother at different collector levels was studied and shown in Fig. 9 - 14. It has been observed that MIBC has no significant effect either with oleic acid or with sodium oleate. Further, experiments were conducted by varying sodium silicate as silica depressant prior to the addition of collector at the best conditions obtained earlier.

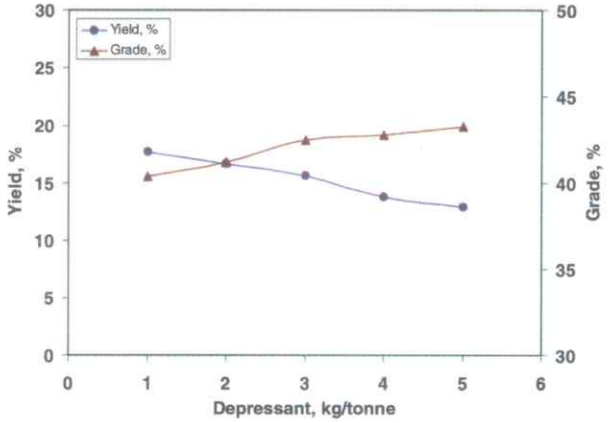

Fig. 15. Effect of depressant

The results of the effect of depressant is shown ion Fig. 15, indicates that better quality concentrate with acceptable can be obtained. As the sodium silicate amount increases, the yield of the concentrate decreases while the grade increases. It has been observed that with 3.0 kg/tonne of sodium silicate and 300 cc/tonne of collector dosage, a cleaner concentrate with 42.50% CaO content can be obtained at a yield of 15.65%.

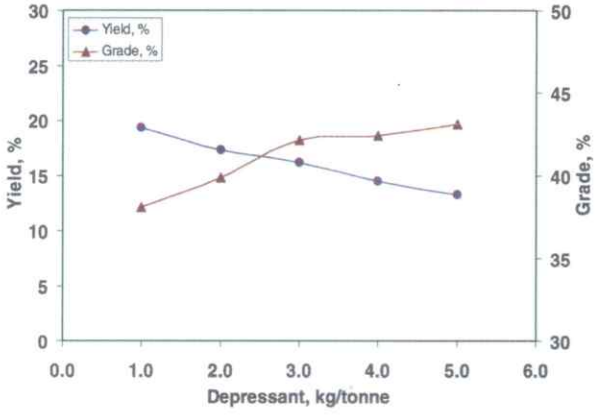

Fig. 16. Effect of depressant with sodium oleate as collector

Attempts are also made to evaluate the effect of depressant with sodium oleate as collector and shown in Fig. 16. It has been observed that with 3.0 kg/tonne of sodium silicate and 2.0 kg/tonne of sodium oleate, a concentrate with 42.16% CaO content can be achieved at a yield of 16.18%. [3]

CONCLUSION

Chemical characterisation study of this lime stone rejects reveals that, the sample contains around 12.09% CaO, 2.95% MgO, 10.73% Al_2O_3, 43.05% SiO_2 and 24.92% LOI. Two stage conventional cell flotation studies indicate that sodium silicate has major role in depressing the gangue and particularly this reject sample responds well to flotation without frother. By using 300 cc/tonne oleic acid as collector and 3.0 kg/tonne of sodium silicate as depressant, it is possible to get a clean concentrate with 42.50% CaO at a yield of 15.65%. Further, with 2.0 kg/tonne of sodium oleate at same depressant dosage, a cleaner concentrate with 42.16% CaO content at an of yield 16.18% can be achieved. The tailings, generated during this process containing 6.41% CaO can be discarded as rejects.

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REFERENCES

[1]. *M.R Patil & M.V. Rudramuniyappa, Beneficiation of low grade limestone of Sahabad area, Gulberg district, Karnataka, Proceeding of the XI International Seminar on Mineral Processing Technology, Jamshedpur, December 15-17, 2010.*

[2]. *Masami Tsunekawa1, Yugo Honma, Kyoungkeun Yoo, Naoki Hiroyoshi and Mayumi Ito, Removal of trace impurity from limestone using flotation techniques. Material Transactions, Vol. 50, No. 1, 2009, pp. 171 - 176.*

[3]. *S.A. Ryemshak, A.A. Adeleke and S. Salami, Characterization of Ubo Limestone for direct burnt lime production. Pacific Journal of Science and Technology, Vol. 13, No. 1, 2012, pp. 661 - 668.*

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WASTE MANAGEMENT IN SUGAR AND DISTILLERY PLANT FOR RESOURCE GENERATION

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ABSTRACT

Sugar industry is one of the most important agro-based industries in India and has important impact on rural economy. India is amongst top two sugar producing countries in the world. There are 527 sugar factories in the country with production of 24.4 MT in 2010-11. India produces about 346.00 MT of sugar cane and 24.20 MT of sugar using 4.88 million hectare land. Total molasses production during 2010-11 was 10.97 MT.

Alcohol is a key feedstock for the manufacture of basic chemicals and presently manufactured in India from molasses. India produces about 2.75 billion liters of alcohol annually. Alcohol based chemical industry occupies an important place in Indian chemical industry and is a key contributor to the growth of the sector and providing alternative feed stock to petroleum base raw material. The current size of alcohol based chemical industry is $1.1 billion (Rs.4850 crores). During the production of sugar and alcohol, large amount of waste is produced which can be utilized for production of value added products. Some of the major wastes from sugar industry are sugar cane leaves, bagasse, bagasse pith, bagasse fly ash from bagasse fired boiler, press mud, molasses and spent wash and fermenter sludge etc. These wastes can be utilized economically for resource generation.

About 0.3 tonnes of bagasse per tonne of sugar is produced which is being used as fuel in the sugar mills. To meet the increasing demand of paper already large numbers of paper mills are in operation for production variety of papers. Amongst various agricultural residues bagasse is most preferred raw material in paper production. Molasses are used for production of alcohol which is being used as important chemical feed stock in addition to its use potable purpose. Bioethanol production from biomass through biochemical route has attracted worldwide attention. Bagasse and bagasse pith can be used as fuel as well for the production of ethanol.. Bagasse fly ash is generated from bagasse fired boiler which is rich in carbon and can be used as adsorbent or for making fire briquette and can also be utilized for making bagasse polymer composite suitable in building materials. Gasification of bagasse to synthetic gas and FT diesel, methanol, Dimethyl Ether (DME) may be another future promising route for value added product from bagasse. Bagasse can also be used as source of furfural.

Biomethanation of spent wash for biogas production is well established and mills producing alcohol are uitilising the gas for power generation. Spent wash contains about 10-12% potassium which can be recovered. About 0.58 kg of CO_2 per litre of alcohol is produced during fermentation of molasses which can be used as feed stock for making large number of chemicals. Press mud (about 4% of cane crushed), fermenter sludge (about 300-400 lit of fermenter sludge per lit of alcohol) can be rich source of nutrient through composting. With installation of R.O. the treatment in distillery plant waste water the reject from membrane can be combined with press mud, fermenter sludge and pith as bio fertiliser.

Key Words: Distillery, Sugar, Alcohol, Bagasse Fly Ash, Molasses

INTRODUCTION

The global sugar industry is one of the world's agricultural based industries, which is estimated to produce around 179 million tons of sugar in the world sugar production during 2010-11 was 168 million tonnes. Estimated world sugar production during 2011-12 and per capita consumption of sugar is given in Figure 1. Sugar industry is one of the most important agro-based industries in India and amongst the top two producing countries in the world and has an important impact on rural economy. India is the fourth largest producer of ethanol in the world and the second largest in Asia. India produces about 2.75 billion litres of The paper presents a critical review for utilistion various by products from sugar and distillery for resource generation which will also help in conservation of huge natural resources.

PROFILE OF INDIAN SUGAR AND DISTILLERY

India is the first two largest sugar producing countries in the world. In 2010-11, sugarcane was planted in 4.98 million hectares across the country, of which 1 million hectares was in Maharashtra and over 2 million hectares in Uttar Pradesh, official estimates show. Uttar Pradesh and Maharashtra are the two largest sugarcane producing states in the country, accounting for more than 80 percent of the annual crop production. India is one of the largest producers of alcohol in the world and there has been a steady increase in its production over the last 15 years, according to fresh statistics. Profile of Indian sugar industries is given in Table 1.

There are 340 distilleries in the country with a capacity of 3,500 million litres. However, the capacity utilization is low mainly due to non-availability of alcohol annually, Chauhan and Dikshit (2011). Most of the distilleries in India are mostly based on sugar cane molasses. Sugar and distillery produces large number of wastes like sugar cane trash, bagasse, bagasse fly ash, bagasse pith, molasses, spent wash, fomenter sludge carbon dioxide, press mud , which can be utilized for producing value added products and will be helpful in improving the economy as well suitable waste management. Further integration of sugar-distillery and paper with minor process modification/ intensification could revitalize these independent industries, Editorial IIChE Journal (2000).

sufficient molasses. The past production of alcohol from the ten major producing states viz. Andra Pradesh, Gujrat, Karnataka, Maharashtra, Tamil Nadu, Uttar Pradesh, Uttarakhand, Bihar, Haryana, and Punjab as shown in chart. Production has been steadily decreasing from 2,500 million litres in FY07 to 1830 million litres in FY10 registering a negative growth of 10 percent pa, Indian chemical industry – XII five year plan (2012-2017).

India is a dominant producer of alcohol in the South-East Asian region with sixty five percent of the total shares and contributes to around seven percent of the total alcohol beverage imports into the region. More than two-thirds of the total beverage alcohol consumption within the region is in India, according to figures in the newly compiled alcohol atlas of India. There has been a steady increase in the production of alcohol in the country, with the production doubling from 887.2 million liters in 1992-93 to 1,654 million liters in 1999-2000 and was expected to treble to 2300 million liters by 2007-08. Alcohol production scenario in India is given in Figure 2.

PROCESS TECHNOLOGY IN A TYPICAL SUGAR AND DISTILLERY PLANT

Sugar Plant

The process of sugar involves following steps (Figure 3)

- Sugar cane transportation to sugar mill after removal leaves etc.
- Milling of sugar cane
- Extraction of juice
- Evaporation of juice
- Juice purification
- Crystallisation
- Refining of the raw sugar.
- Power generation using bagasse

ALCOHOL FROM MOLASEES

Molasses is the residue left after extraction of crystallised sugar and is one of the major byproducts of the sugar industry. Ethyl alcohol is made from molasses by fermentation process utilising yeast enzymes. A typical alcohol manufacturing process include (Figure 4).

- Molasses handling
- Fermentation feeding system
- Preparation of yeast inoculums, propagation of yeast
- Fermentation
- Distillation of dilute alcohol for removal of impurities
- Concentration of the dilute alcohol to rectified spirit and absolute alcohol

WASTE GENERATION AND UTILIZATION IN SUGAR AND DISTILLERY PLANTS

Sugar mills produce wide range of byproducts along with generation of wastewater, air pollution, noise pollution, and odor. The Various by-products generated from sugar mills are Sugar Cane Trash, Bagasse, Bagasse Pith, Bagasse Fly ash, Molasses, Press Mud which can be used for resources generation. Various sugar mill wastes and their potential ustilisation are given in Table 2. Distillery produces wide range of byproducts along with generation of wastewater, air pollution, noise pollution, and odor. The Various byproduct generated from distillery are spent wash, carbon dioxide, fermenter sludge, which can be used for resources generation. Various distillery wastes and their ustilisation are given in Table 3. Product profiles of distillery are shown in Figure 5.

Integration of paper-sugar-distillery industries with introduction of minor process modification/intensification could revitalize these interdependent industries. Integration of sugar, distillery and paper manufacturing and waste utilization is given in Figure 6.

India producing nearly 357 million tonnes per annum and nearly 60 percent of the cane is utilized for the production of sugar of which about $1/3^{rd}$ of the total sugar cane is obtained as residue so called bagasse containing appreciable quantity (upto 35 percent by weight) of the pith, Jain et al.(2011). This bagasse can be used for the manufacture of alcohol. Bagasse is also a promising biomass for the production of alcohol and as substitute for convention fuels. Bagasse can be also used for production of furfural which has wide scope as solvent as well as starting material for large number of resins. The option for new herbicides production starting from furfural has been also studied, Almazan et al.(1998). Bagasse is also rich source of hemicelluloses. Some of the materials derived from hemilceloose find application in packaging film, food coatings, cationic biopolymers, hydroigels and biomedical uses Sabina-hanim & Siti-Norsafurah (2012).

Utilisation of Bagasse as Sustainable Raw Material for Paper Making and Rayon grade Pulp

Although bagasse produced by sugar mills are used as fuel, however bagasse because of its good fibre properties

compared to other agricultural residues, it is being used as replacement of forest based raw material hardwood, bamboo and is considered best alternative fibre amongst the agricultural residues due its low quality, cost and renewable nature. Some of the major constrain in its utilization is the seasonal availability of bagasse requiring storage of large quantities of bagasse. Bagasse based pulp has superior properties than the other agro based pulp like wheat straw and rice straw. With estimated projection of paper and board production of 20 million tonnes in India by 2020 from existing 11 million tonnes, bagasse can play important role in meeting demand of agro based pulp. The use of non wood raw material is increasing and at present about 61 percent of the total production is based on non-wood raw material. Viscose rayon is playing important role in man-made fibre industry. Cellulose from rayon grade pulp from bagasse can be another promising use of bagasse.

Bagasse Fly Ash in Waste Water Treatment

Bagasse fly ash is generated during combustion of bagasse in the boiler. Approximately 0.97 million tonnes of unburned carbon is available from bagasse fly ash in India, Balkrishna & Batra (2011). Bagasse fly ash along with metal oxides contains unburnt carbon. Typical characteristics of bagasse fly ash are given in Table 4. Utilization of bagasse fly ash has been explored as adsorbent and has been found very effective in removal heavy metals, dyes, color, picoline and pyridines and other refractory organics like phenols, chlorophenols and for removal of COD from large number of industrial wastes and also from dairy, Kushwaha et al.(2010); Lataye et al.(2008); Lataye et al.(2008); Lataye et al.(2011); Lowenheim & Moran (1975); Mall et al.(2006); Mall et al.(2011); Mall et al.(1994); Mall et al.(2005); Mall et al.(2005); Mall et al.(2007); Srivastata et al.(2006); Srivastata et al.(2007); Srivastata et al.(2006); Swamy et al.(1997); Swamy et al.(1998); Sahu et al.(2008); Mane et al.(2007). Various types of waste water treated using bagasse fly ash is given in Table 5.

Bagasse Fiber Composite for Building Applications

Wood is an important building material used in numerous applications in building industry. It is very difficult to replace wood by a single alternative material. So its alternative can be natural fibre reinforced composites with variety of matrix materials (organic and inorganic both), which are cost effective, energy saving and good wood alternatives. Here the developed composites using bagasse fibre with poly-vinyle chloride (PVC), low density poly-ethylene virgin (LDPE-V) and low density poly-ethylene waste (LDPE-W) are described briefly. In all the developed composites, used bagasse fibre is obtained by pulping of bagasse with soda process.

The developed composites meets mostly the requirements of medium density fiber composites as laid down IS:3087-1985 entitled specifications for wood particle boards (medium density) for general purposes. The comparative results of all the three polymeric composites are given in Table 6, Mall et al.(2006); Agrawal (2009); Agrawal et al.(2003).

CONCLUSIONS

The waste generated from sugar and distillery can provide an attractive means of resource generation and can provide number of value added applications. Bagasse is seen as future raw material for paper mills as well as rayon grade pulp. Although extensive work has been done for utilisation of bagasse fly ash as adsorbent bagasse can be promising source of biofuel and energy and substitute of coal and petroleum. Alcohol a major product of distillery produced from molasses is again seen as future raw material for chemical industry.

REFERENCE

1. *Agrawal, S.P. Mall, I.D. Agrawal, C.P. and Verma, C.L.(2003) Filler additives: "Effect on PVC composites: Chem.Engg.World July, 79-83.*
2. *Agrawal, S.P.(2009) Studies on Polymer-bagasse fibre composite for application as building material, Ph.D Thesis, IIT Roorkee, India*
3. *Almazan, O. Gonzalez, and Galvez, L.(1998) The sugarcane, its by-products and co-products. AMAS 1998. Food and Agricultural Research Council, Reduit, Mauritius*
4. *Balakrishnan, M. and Batra, V.S.(2011) Valorization of solid waste in sugar factories with possible application in India: A review. J. of Envir.Management 92, 2886-2891*
5. *Chauhan, M.S. and Dixit, A.K.(2001) International Conference on Future Environment and Energy IPCBEE vol 28,119-123*
6. *Gehlawat, J.K.(1992) Souveir; All India Seminar on Effluent treatment, Pollution Control and Byproduct Utilization in Sugar Industry and Distilleries. Organized by the Institution of Engineers (India) Andhra Pradesh State Centre. pp. 54*
7. *Iyer, P.V.R. Rao, T.R. and Grover, P.D.(2002) Biomass Thermo-chemical characterization, third edition. IIT New Delhi*
8. *Jain, R.K. Thakur, V.V. Diwakar, P. Adhikari, D.K. Dixit, A.K. and Mathur, R.M.(2011) Bioethanol from Bagasse pith a lignocellulosic waste biomass from paper/ sugar industry. IPPTA J. Vol. 23, No. 1.*
9. *Kaul, S.N. Pathe, P.P and Nandy, T.(1990) An overview of waste management in sugar Industry. J IAEM vol 17 (15), pp.55.*
10. *Kushwaha, J.P. Srivastava, V.C. and Mall, I.D.(2010) Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: Parametric, kinetic and equilibrium modelling, disposal studies. Bioresource Technology. Vol. 101, pp. 3474–3483.*
11. *Lataye D.H., Mishra I.M., and Mall I.D.(2008) Adsorption of 2- picoline onto bagasse fly ash from aqueous solution. Chemical Engineering Journal, Vol. 138, pp.35-46.*
12. *Lataye, D.H. Mishra, I.M. and Mall, I.D.(2008) Multicomponent sorptive removal of toxics-pyridine, 2-picoline and 4-picoline- from aqueous solution by bagasse fly ash: Optimization of process parameters. Industrial and Engineering Chemistry Research 47(15) pp.5629-5635.*
13. *Lataye, D.H. Mishra, I.M. and Mall, I.D.(2011) Removal of 4-Picoline from Aqueous Solution by Adsorption onto Bagasse Fly Ash and Rice Husk Ash: Equilibrium, Thermodynamic and Desorption Study. ASCE: Journal of Environmental Engineering. Vol. 137, No. 11, , pp. 1048-1057*
14. *Lowenheim, F.A. and Moran, M.K.(1975) Faith, keyes & Clarks Industrial Chemicals, 4th edition, Wiley Interscience Publication, New York.*
15. *Mall I.D.(1995) Waste utilization and management in sugar and distillery plants, Chemical Engineering World vol. 30 (1) pp. 51-60.*
16. *Mall, I.D. Agarwal, C.P. Negi, Y.S. and Agrawal, S.P.(2006) Effect of fibre loading on Bagasse Fibre – PVC Composites. Internation Journal of Plastics Technology vol. 10, pp. 655 – 664.*
17. *Mall, I.D. Lakshmi, U.R. and Srivastava, V.C.(2011) Removal of indigo carmine dye from aqueous solution using bagasse fly ash. WITS (Water & Sustainable Economic Development) Conference held at the FAAP University, Sao Paulo, BRAZIL, pp.17-19.*
18. *Mall, I.D. Mishra, N. and Mishra, I.M.(1994) Removal of Organic Matter from Sugar Mill Effluent using Bagasse Flyash Activated Carbon. Research and Industry, Vol. 39, pp.115.*

19. *Mall, I.D. Srivastava, V.C. Agarwal, N.K. and Mishra, I.M.(2005) Adsorptive Removal of Malachite Green Dye from Aqueous Solution by Bagasse Fly Ash and Activated Carbon- Kinetic Study and Equilibrium Isotherm Analyses. Colloids and Surfaces, A: Physicochemical and Engineering Aspects, vol. 264, pp.17-28.*
20. *Mall, I.D. Srivastava, V.C. Agarwal, N.K. and Mishra, I.M.(2005) Removal of Congo Red from Aqueous Solution by Bagasse Fly Ash and Activated Carbon: Kinetic Study and Equilibrium Isotherm Analyses. Chemosphere, vol. 61, pp. 492-501.*
21. *Mane, V. Mall, I.D. and Srivastava, V.C.(2007) Use of Bagasse Fly Ash as an Adsorbent for the Removal of Brilliant Green Dye from Aqueous Solution. Dyes Pigments, vol.73, pp. 269-278.*
22. *Mckay, G.M. El Grundi, M. and Nassar, M.M.(1988) External mass transport processes during the adsorption of dyes onto bagasse pith. Water Res, vol. 22, pp. 1527-1533*
23. *Panesar, P.S. Prasad, B., and Kumar, P.(1992) Souveir Effluent treatment, Pollution Control and Byproduct Utilization in Sugar Industry and Distilleries, All India Seminar, Organized by the Institution of Engineers (India) Andhra Pradesh State Centre , pp. 54*
24. *Pessoa, J.A. Manchilha de, I.M. and Sato, S.(1997) Evaluation of Sugarcane hemicelluloses hydrolyzate for cultivation of years and filamentous fungi. Journal of Industrial Microbiology and Biotechnology, vol.18, pp.360-363*
25. *Rao, N.(1992) Souveir: Effluent treatment, Pollution Control and Byproduct Utilization in Sugar Industry and Distilleries, All India Seminar, Organized by the Institution of Engineers (India) Andhra Pradesh State Centre, pp. 60.*
26. *Sabiha-Hanim, S. and Siti-Norsafurah, A.M.(2012) Physical properties of hemicelluloses films from sugar cane bagasse. Procedia Engineering42,1518-1523*
27. *Sahu, A.K. Mall, I.D. and Srivastava, V.C.(2008) Studies on the adsorption of furfural from aqueous solution onto low-cost bagasse fly ash. Chemical Engineering Communications, vol. 195, pp. 316–335.*
28. *Singh, P. Sman, A. Tiwari, P. Arya, Gaur. N. and Srivastava, A.K.(2008). Biological pretreatment of sugarcane trash for its conversion to fermentable sugars. World Journal of Microbiology and Biotechnology, vol.24, pp.667-673.*
29. *Srivastava, V.C. Mall, I.D. and Mishra, I.M.(2006) Competitive antagonistic adsorption of nickel(II) and zinc(II) metal ions from aqueous solution onto bagasse fly ash, 11th APCChE congress, Asian Pacific Confederation of Chem. Eng., Kuala Lumpur, Malaysia, pp.27-30.*
30. *Srivastava, V.C. Mall, I.D. and Mishra, I.M.(2007) Multi-Component Adsorption Study of Metal Ions onto Bagasse Fly Ash using Taguchi's Design of Experimental Methodology. Industrial & Engineering Chemistry Research vol. 46, pp. 5697-5706.*
31. *Srivastava, V.C. Swamy, M.M. Mall, I.D. Prasad, B. and Mishra, I.M.(2006) Adsorptive Removal of Phenol by Bagasse fly ash and Activated Carbon: equilibrium, kinetics and thermodynamic study. Colloids and Surfaces, A: Physicochemical and Engineering Aspects 272, pp. 89-104.*
32. *Swamy, M.M. Mall, I.D. and Prasad, B.(1997) Resorcinol Removal Aqueous Solution by Bagasse Fly Ash and Activated Carbon, IE(I) J. EN, vol.77, pp. 49.*
33. *Swamy, M.M. Mall, I.D. Prasad, B. and Mishra, I.M.(1998) Sorption Characteristics of O-Cresol on Bagasse Fly Ash and Activated Carbon, Indian J. of Environmental Health, vol. 40, pp. 67-78.*

34. *Vivek, K.(1993) Removal of Organic Matter from Distillery effluent Using Adsorption, M.E. Dissertation, Dept. of Chemical Enng. Univ. of Roorkee.*

35. *Yadav, R.L. and Solomon, S.(2006) Potential of developing sugarcane by-product based industries in India, Sugar Technology, vol. 8, pp.104-111.*

Table 1 Profile of Indian Sugar Industry

Particulars	2006-07	2007-08	2008-09	2009-10	2010-11
No. of Factories in Operation	501	516	488	490	527
Cane Production (000 Heactares)	5151	5055	4415	4175	4885
Sugar Production (000 Tonnes)	28328	26356	14538	18912	24394
Molasses Production (000 Tonnes)	13089	11213	6542	8400	10970

As per 2010-11		
Area	**Cane Production**	**Sugar Production**
4.98 Million Hectares	346.00 Million Tonnes	24.20-24.50 Million Tonnes

Sources: Indian Sugar Mill Association; http://www.indiansugar.com/Statics.aspx [Open on: 8 nov. 2012]; Business standard April 24, 2012

Table 2 Sugar Mill Waste Generation and Utilization

Waste	Generation	Characteristics	Utilization
Sugar Cane Trash	0.09-0.11 ton trash per ton of sugarcane harvested		Generation of Power, Cattle Feed or Fodder
Bagasse	0.25 – 0.30 tonne of bagasse per tonne of sugarcane	Cellulose-36.4%, Hemicellulose-18.2%, Lignin-22.8%. Calorific Value: 3000 kcal/kg Moisture: 47-50% Fibrous Material: 55.0% Pith: 34.3% Water Souble: 10.7%,	Generation of Steam and Power Alcohol Gasification for synthesis gas and fuel, Bagasse pulp for paper and news print Bagasse cellulose for rayon, Polymer Bagasse Fibre Composite, hemicellose, herbicide
Bagasse Pith	Around 0.5 tonnes per tonee of bagasse based paper	Cellulose-46%, Hemicellulose-22%, Lignin-21.8%.	For treatment of wastewater Alcohol production
Bagasse Fly ash	0.005 – 0.066 ton fly ash per ton of sugarcane crushed	%,Bulk density: 244 g/m^3 Moisture: 8.11% Volatile Matter: 22.46 % Ash: 30.74 % Fixed Carbon: 46.80 %	Treatment of sugar, distillery and mixed sugar and distillery effluent.
Press Mud	0.03 ton per ton cane processed	P_2O_5: 4470 mg/L K_2O_5: 4500 mg/L CaO: 10,500 mg/L MgO: 6450 mg/L Wax: 9% Moisture: 76%	Manufacture of carbon paper, shoe polish, wax paper, Manure, Land fill, substitute of raw material for cement

Molasses	0.4 tonnes of molasses per tonne of sugar	TDS: 2,00,000-3,10,000 mg/L BOD_5: 4,20,000 mg/L COD: 9,45,000 mg/L Chlorides: 30,000 mg/L Sulfates: 15,000 mg/L	Production of alcohol and cattle feed, foundries and manufacture of citric acid

Sources: Balakrishnan and Batra, 2011; Mall, 1995; Singh et al., 2008a; Pessoa et al., 1997; Jain et al., 2011; Agrawal, 2009; Jain et al., 2011; Iyer et al., 2002; Mckay et al., 1987; Panesar et al., 1992; Mall et al., 2005, 2006, 2011; Yadav and Solomon, 2006; Kaul et al., 1990; Vivek, 1993; Mall and Varshney, 1992

Table 3 Distillery Waste Generation and Utilization

Waste	Generation	Characteristics	Utilization
Spent Wash	5-20 lit / lit of alcohol	COD: 91,740 mg/L BOD_5: 40,532 mg/L TOC: 19,357 mg/L TS: 78,684 mg/L SS: 19,434 mg/L DS: 57,250 mg/L Iron: 62 mg/L Chloride: 35,000 mg/L	Fertilizer or as animal feed supplement, compost
Carbon Dioxide	0.58 kg/lit of alcohol		The gas generated are purified and made available to consumer
Fermenter Sludge	300-400 kg/lit of alcohol		Manure

Sources: Balakrishnan and Batra, (2011); Mall(1995) Gehlawat, 1992

Table 4 Characteristics of the Bagasse Fly Ash

Adsorbent	(BFA)
Inherent Moisture (%)	3.63
Ash (%)	73.36
Volatile Matter (%)	2.34
Fixed Carbon (%)	20.67
CHN Analysis	
Carbon (%)	16.36
Hydrogen (%)	9.77
Nitrogen (%)	2.55
BET Surface Area	
Average pore dia(A^0)	23.97
BET Surface Area	168.39 m^2/g
Heating value(kJ/kg)	4631.6

Table 5 Treatment of Various Types of Waste Water Using Bagasse Fly Ash

Phenols	Phenol, Resocinol, o-cresol, Chlorinted phenols, tetra chlorocatechol-, Cresol,
Pyridine and picoline	Pyridine and 2, 4 Picoline, Amino pyridine
Dyes	Methyl voilet, Rhodamine dye Methylene blue, Scarlet, Malachite green, Metanil yellow, Congored, Auramine, Orange G, Acid orange
Industrial waste	Agro based pulp and paper mill, large integrated pulp and paper effluent , Polyester plant waste, Sugar and distillery plant waste, Phenol formaldehyde resin plant waste, Electroplating waste Dairy waste water,

Source: Kushwaha et al., 2010; Lataye et al., 2008; Lataye et al., 2008; Lataye et al. 2011 Lowenheim and Moran, 1975; Mall et al., 2006; Mall et al., 2011; Mall et al., 1994; Mall et al., 2005; Mall et al., 2005; Mall et al., 2007; Srivastata et al., 2006; Srivastata et al., 2007; Srivastata et al., 2006; Swamy et al., 1997; Swamy et al., 1998; Sahu et al., 2008; Mane et al., 2007

Table 6 Comparative Characterization Results of Composites with IS:3087-1985

Property	**Values as per IS:3087**	**Values for Composites as Determined**		
		Matrix Material/ (Bagasse Content-wt %)		
		PVC (60%)	**LDPE-V (20%)**	**LDPE-W (40%)**
Specific Density	0.5-0.9	1183.97	1013.40	998.49
Initial Moisture, %	Not given	1.845	0.337	1.321
Water absorption, %				
-2 hrs soaking	25	2.184	2.170	3.537
-24 hrs soaking	50	7.696	2.310	4.372
Change in dimensions due to 2 hrs soaking in water, %				
-Thickness	10	0.071	0.078	0.076
-Length	0.5	0.210	0.073	0.0473
-Width	0.5	0.210	0.073	0.0473
Tensile strength perpendicular to surface, kg/cm^2	8.0	8.719	8.227	8.005
Tensile strength parallel to surface, kg/cm^2	Not given	90.099	66.581	80.520

Sources: Mall et al., 2006; Agrawal, 2009; Agrawal et al., 2003

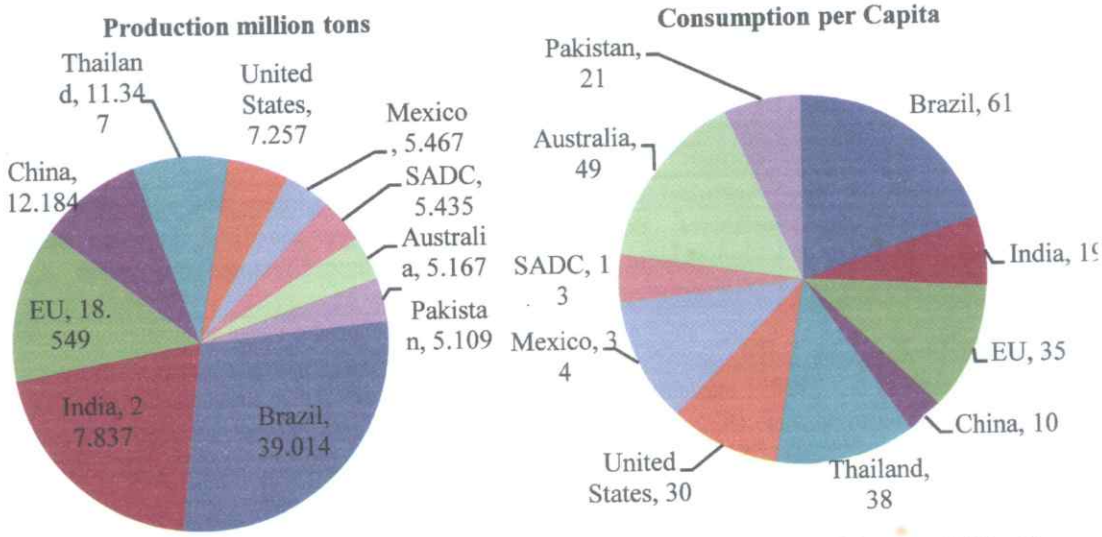

Figure 1 World Sugar Production and per capita Consumption of during 2011-12

Source: http://www.illovosugar.co.za/World_of Sugar/Sugar_Statistics/International.aspx (Open on 11 Nov 2012)

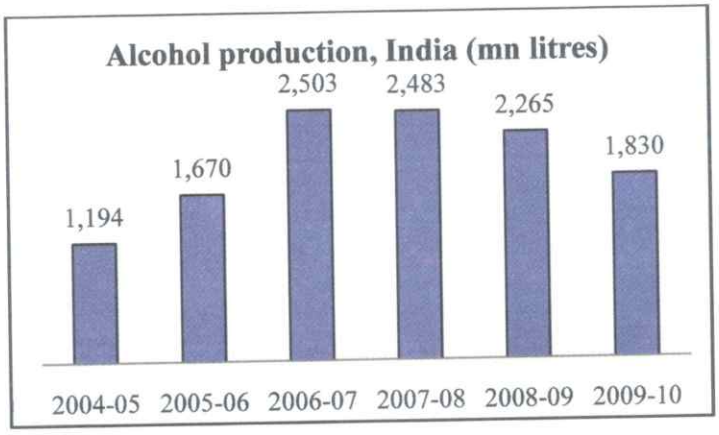

Figure 2 Alcohol Productions in India

Sources: Indian chemical industry – XIIth five year plan 2012-2017

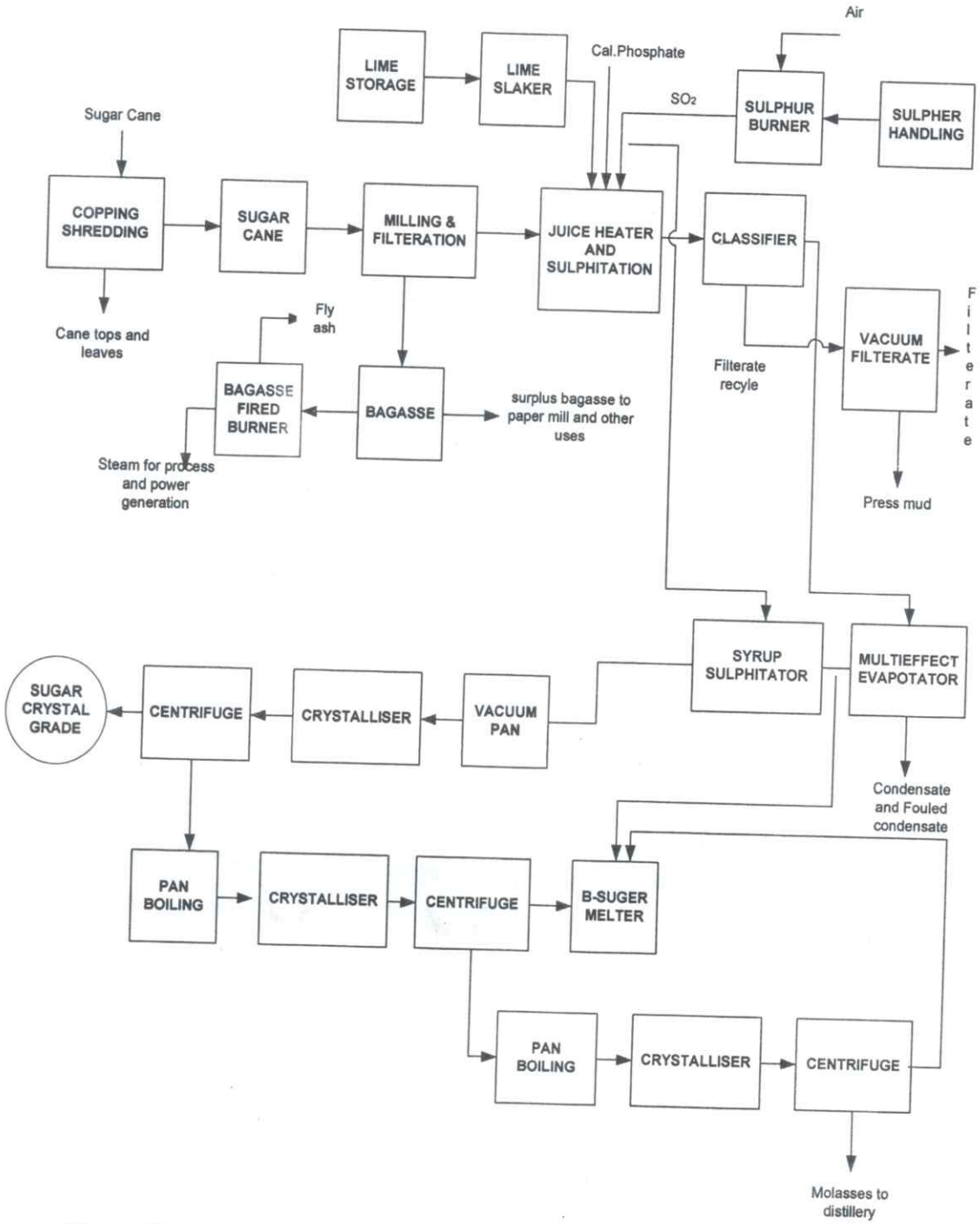

Figure 3 Process of Sugar Manufacture and Source of Waste Generation

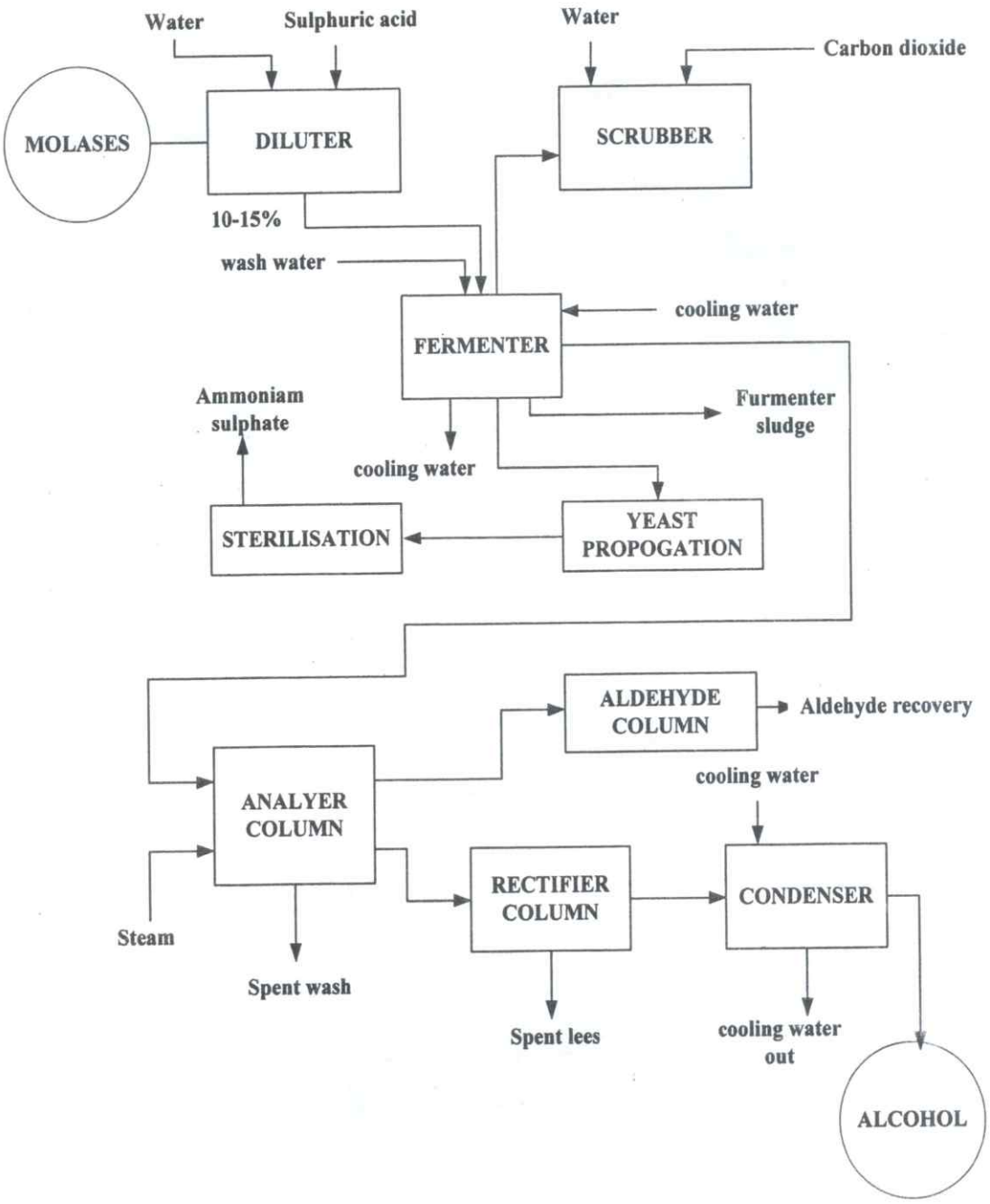

Figure 4 Process of Manufacturing of Alcohol

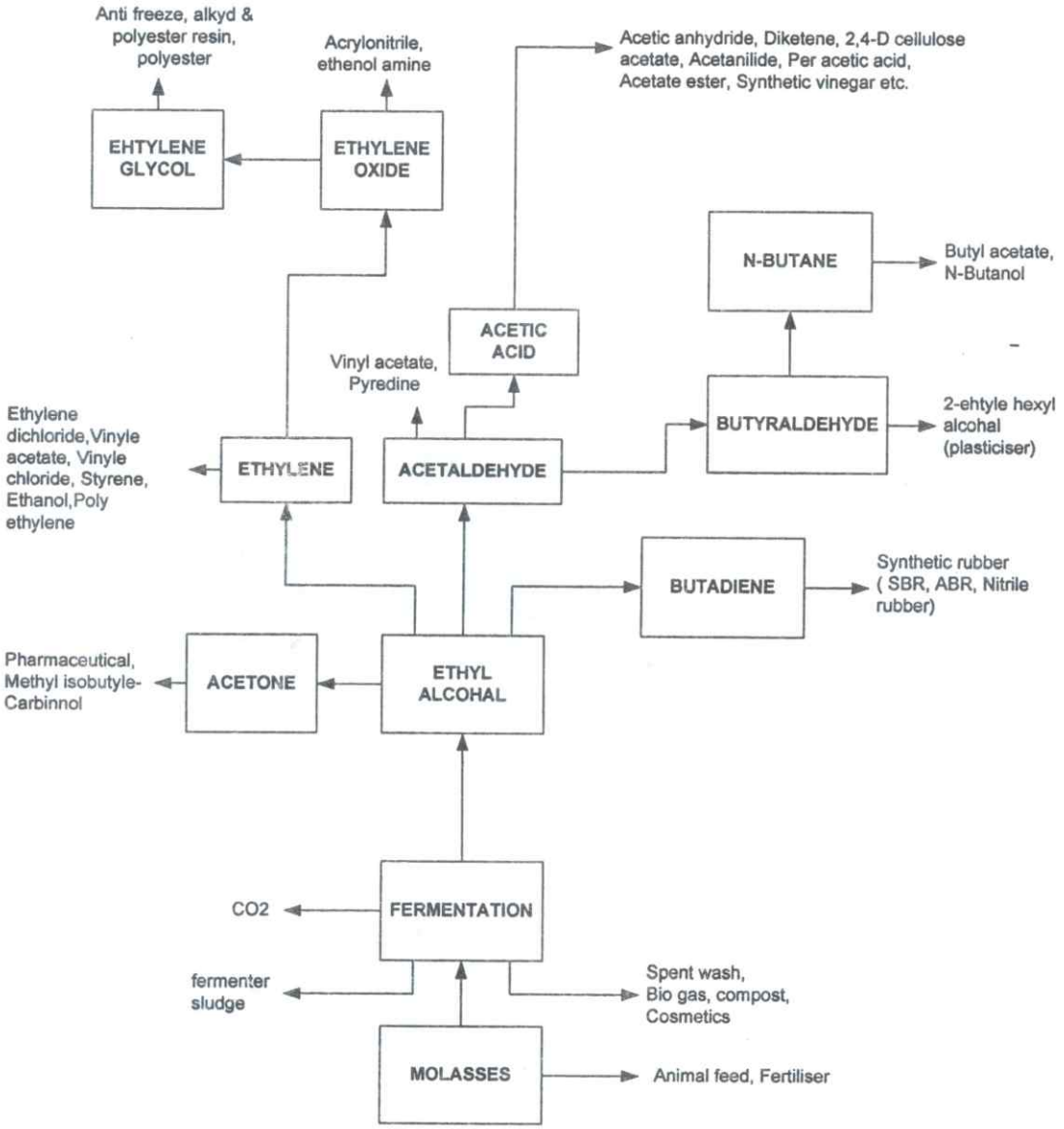

Figure 5 Product Profiles of Distillery Plant
Source: Mall (1995)

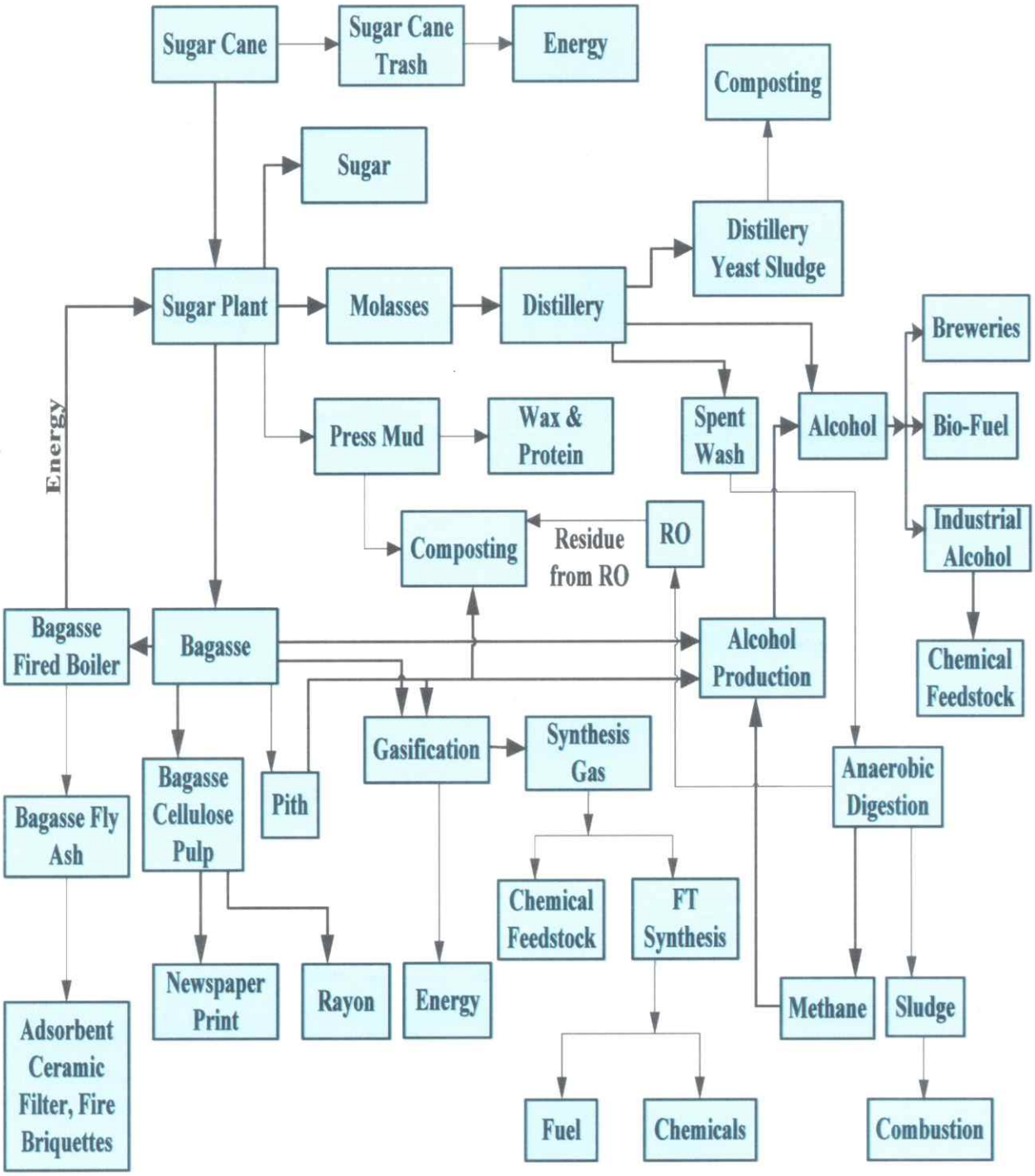

Figure 6 Integration of Sugar, Distillery and paper Manufacturing and Waste Utilization

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RECYCLING OF SOLID WASTE GENERATED IN THE STEEL PLANT THROUGH EXTRUSION

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ABSTRACT

Iron bearing byproducts generated during different stages of iron and steel production needs to be agglomerated for its reuse owing to its fine size. The traditional way of recycling them into iron making furnaces has been through pelletizing, sintering, briquetting etc. But these materials, when used as fines in high proportions, adversely affect the quality thereby restricting their usage. Hence, a need arises to develop a techno-economic viable and environmentally safe method for agglomerating iron-rich steel plant byproducts. In the process of extrusion, various iron bearing byproducts, carbonaceous material and other waste materials generated can be agglomerated using suitable binder(s) for charging into iron making furnaces. At JSW Steel, various solid wastes such as Mill Scale, CRM (Cold Rolling Mill) oxide, BOF (Basic Oxygen Furnace) sludge etc. rich in Fe are generated. A laboratory scale single screw extruder has been designed and developed at R&D Centre of JSW Steel Ltd. to agglomerate the solid wastes. In order to produce desired strength, studies have been carried out to select a suitable binder. Using the iron bearing byproducts in different proportions, the extruded product was analyzed for physical and chemical properties to decide its suitability and usage. The laboratory results are found encouraging and in the acceptable range.

Key words: Steel plant wastes, Single screw extruder, CCS, Tumbler Index

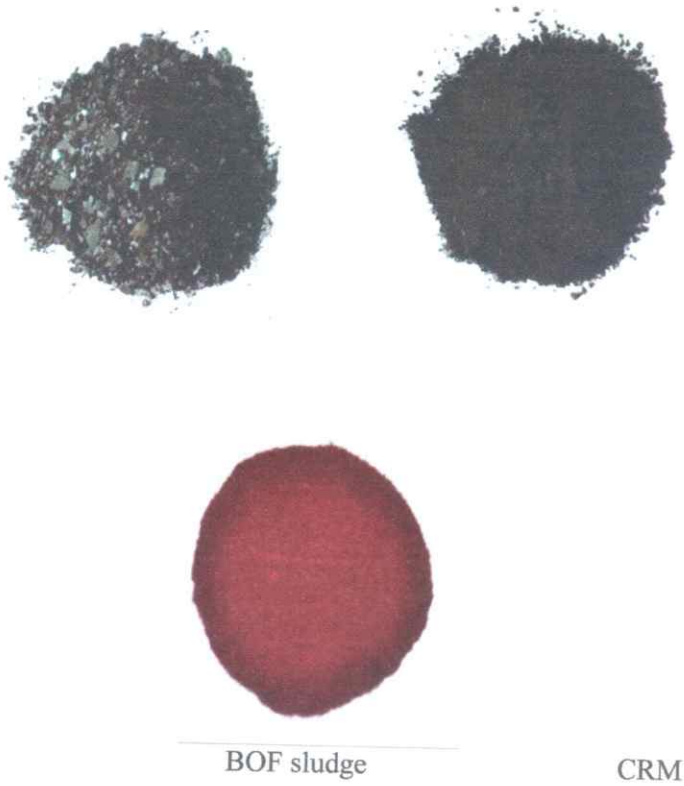
INTRODUCTION

In Integrated Steel Plant (ISP), a number of iron bearing byproducts are generated during various stages of iron and steel production. These materials, when used as fines in high proportions, adversely affect the quality thereby restricting their usage. The traditional way of recycling them into iron making furnaces has been through pelletizing, sintering, briquetting etc. For agglomerates to be considered as suitable feed material to furnace, they should have sufficient strength for handling, transportation and good reducibility without much degradation. The process for producing such agglomerates should be robust enough to tolerate a variety of materials in different proportions, economically viable even at relatively small scale operations with little or no pollution. In present work, a novel technique of extruding the waste using suitable binder(s) has been considered as a feasible option. In this process, various iron bearing byproducts, carbonaceous materials and other waste materials can be agglomerated using binder(s) into a form, suitable for charging into iron making furnaces. A laboratory scale single screw extruder has been designed and developed at R&D Centre of JSW Steel Ltd. to agglomerate the solid wastes. Iron rich wastes generated at JSW are shown in Table 1.

Table 1: Iron rich waste generation at JSW.

Type of solid waste	Quantity (tons per day)
BOF sludge	230
Mill Scale	375
CRM oxide	30

Mill scale is generated at caster and rolling mills and is presently being used in sinter making. BOF sludge is generated at SMS after wet scrubbing process and is presently being used in pellet making. CRM oxide is generated after pickling at CRM and is presently selling to the paint industries.



Mill Scale BOF sludge CRM oxide

Fig. 1: Images of various Iron rich wastes generated at JSW.

Several studies have been carried out on recycling of steel plant waste into iron making furnaces through cold bonded agglomeration. Bogdan et.al[1] used Portland cement and bentonite in the range of 10-15% with revert materials such as finishing mill scale, steelmaking slag and blast furnace flue dust. Investigation by Lotosh et.al[2] made use of ordinary Portland cement as binder. These pellets were found suitable for use in blast furnace in limited quantities. The pellets were prepared using 9-10% cement followed by curing under normal humid conditions for ~28 days to attain crushing strength of around 130 kg/pellet. Hoffken et.al[3] of Thyssen had reported that steel plant dust can be briquetted at ~750 °C without using any binder. Studies carried out by Maneesh[4] on cold briquetting indicated that these briquettes can be used in blast furnaces in small proportions.

Single Screw Extruder

Figure 2 shows a continuous type single screw extruder developed at JSW jointly by R&D and Central repair shop. Lab scale studies have been carried out to select the suitable binder and produce extruded pellets through extrusion process using various wastes.

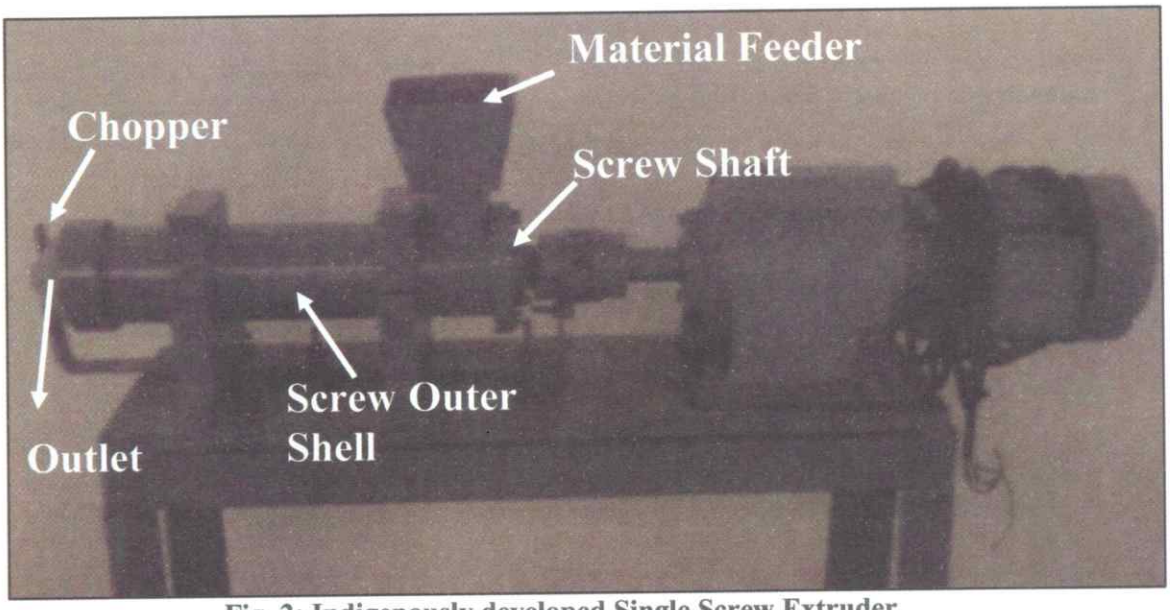


Fig. 2: Indigenously developed Single Screw Extruder.

EXPERIMENTAL

I. Raw materials: The iron bearing waste generated in the plant was used in laboratory trials. Table 2 shows the typical chemical and size analyses of various iron-rich wastes generated at the plant. The laboratory experiments have been conducted using Mill scale, BOF sludge, Iron Ore Fines (IOF), CRM Oxide etc. in varying proportions with starch and bentonite as binders. Trials were done initially with 100% pellet grade iron ore fines and then decreased proportionately upon addition of other materials. Table 3 shows the proportion of various raw materials used in laboratory studies. The raw materials were ground up to below 100 mesh(#) size.

Table 2: Properties of Iron rich waste generated at JSW.

	Iron ore fines (Pellet grade)	Mill Scale	BOF Sludge	CRM Oxide
Chemical analysis, %				
Fe (t), %	63.0	66.7	50.9	75.0
SiO_2, %	4.0	-	2.73	0.2
Al_2O_3, %	2.2	-	1.24	0.2
CaO, %	-	0.40	15.0	-
C, %	-	0.13	1.2	-
Size analysis				
+100 #, %	5.0	85	8.1	0.0
-100 to + 200#, %	20.0	15	20.5	3.2
-200 to +325 #, %	25.0	-	14.9	4.5
-325 #, %	50.0	-	56.5	92.3

II. Preparation of Extruded Agglomerates:

Studies were carried out for the optimization of binder quantity to be used in extrusion. A batch of 10 kg mix was used in each trial. Based on the results obtained, binder percentage and iron bearing materials combination were varied. Moisture was maintained 12%. The thoroughly mixed material (dough) was then put into the extruder for producing agglomerates. The green extruded product subjected to curing in hot air oven for 2 hrs at 180 °C. In present work, extruded pellets were prepared using existing plant wastes. Further studies can be done by reducing the same in a rotary hearth furnace (RHF) and the product DRI (Direct Reduced Iron) can be used in Iron and steel making units. Figure 3 shows the flow sheet for producing extruded agglomerates and its usage.

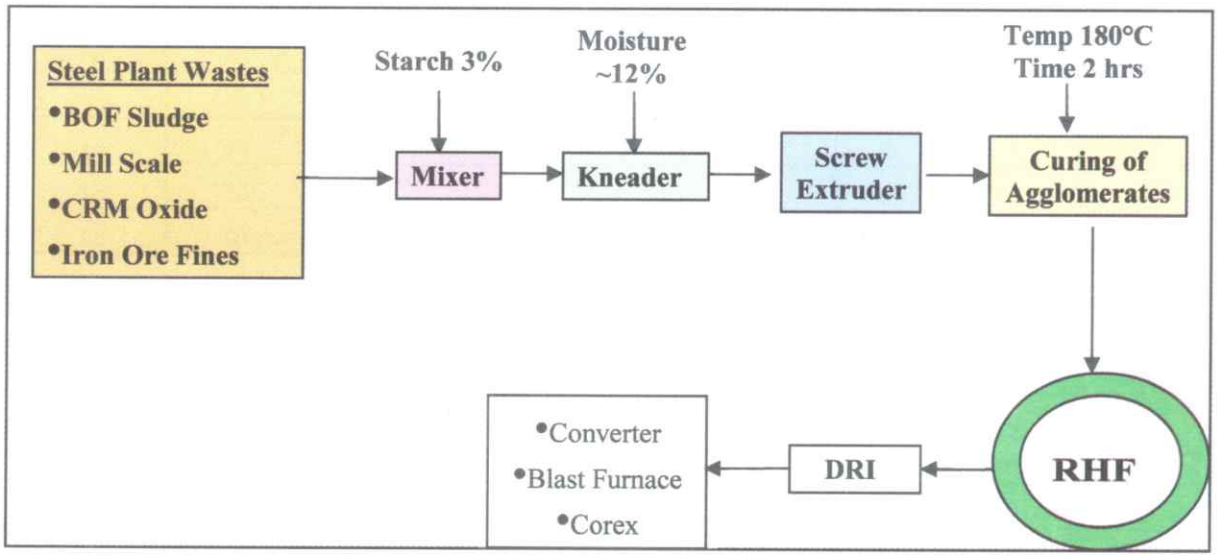


Fig. 3: Flow sheet for producing extruded agglomerates.

RESULTS AND DISCUSSION

The extruder agglomerates were prepared with 100% Iron Ore Fines (IOF) initially, bentonite and starch as binders.

Table 3: Raw materials proportion and strength parameters of extruded pellets.

Expt. No.	Iron Ore Fines, %	Mill Scale, %	BOF Sludge, %	CRM Oxide, %	Starch, %	Bentonite, %	Fe (total), %	CCS, kg/pellet	Tumbler Index (TI) +6mm, %
1	100	0	0	0	5	3	63	18	23
1	100	0	0	0	4	4	63	21	25
2	100	0	0	0	5	0	63	68	82
3	100	0	0	0	4	0	63	63	80
4	100	0	0	0	3	0	63	41	50
5	25	25	25	25	4	0	67	15	19
6	50	0	25	25	5	0	64	40	51

Expt. No.	Iron Ore Fines, %	Mill Scale, %	BOF Sludge, %	CRM Oxide, %	Starch, %	Bentonite, %	Fe (total), %	CCS, kg/pellet	Tumbler Index (TI) +6mm, %
7	100	0	0	0	4	0	63	53	64
8	90	0	10	0	4	0	63	51	74
9	80	0	20	0	4	0	63	45	52
10	70	0	30	0	4	0	63	16	20
11	75	10	15	0	5	0	64	69	85
12	65	20	15	0	5	0	65	54	65
13	55	30	15	.0	5	0	66	61	72
14	45	40	15	0	5	0	68	52	62
15	45	30	25	0	5	0	66	65	78
16	35	40	25	0	5	0	68	64	77
17	35	30	35	0	5	0	66	61	71
18	25	40	35	0	5	0	67	61	72
19	20	40	40	0	5	0	67	62	75
21	0	40	60	0	5	0	67	55	63
22	0	40	50	10	5	0	68	35	49
23	100	0	0	0	5	0	63	54	61
20	**10**	**40**	**50**	**0**	**5**	**0**	**67**	**63**	**84**
24	10	40	50	0	5	0	67	61	82
25	10	40	50	0	4	0	67	62	81
26	**10**	**40**	**50**	**0**	**3**	**0**	**67**	**60**	**83**
27	10	40	50	0	2	0	67	56	66
28	10	40	50	0	1	0	67	35	48

IOF alone is giving desirable Cold Crushing Strength(CCS) and Tumbler Index (TI) where as CRM oxide was used up to 25% but could not achieve the desirable strength. Table 3 indicates that the strength decreased with use of bentonite as binder.

By fixing the starch at 5%, the best obtained results, the raw material IOF was replaced with BOF sludge and Mill Scale. It was observed that BOF sludge can be increased up to 50% without affecting the strength. It was also observed that with increase in Mill Scale the strength increased up to 50%. With the combination of 50% BOF Sludge + 40% Mill Scale + 10% IOF (Blend-J) achieved the highest physical properties like Cold Crushing Strength (CCS) of 63kg/pellet and TI +6.3 mm of 84%. Keeping the above composition constant the starch has been optimized by varying from 1-5%. It was observed that minimum desired strength obtained with starch more than 3%.

The best properties of extruded agglomerates was obtained using a combination of 50% BOF sludge, 40% mill scale and 10% IOF with 3% starch as a binder which produced CCS of 60 kg/pellet and tumbler index (+6.3 mm) of 83%.

Figures 4 and 5 represent the results of trials conducted using blend-J (highlighted in Table 3) by varying starch content.

Figure 4 shows that the cold crushing strength of extruded pellets increased up to the usage of 3% starch as binder. Fig. 5 shows that TI (+6.3mm) of the extruded pellets increases with the binder (starch) up to 3 % and thereafter becomes constant.

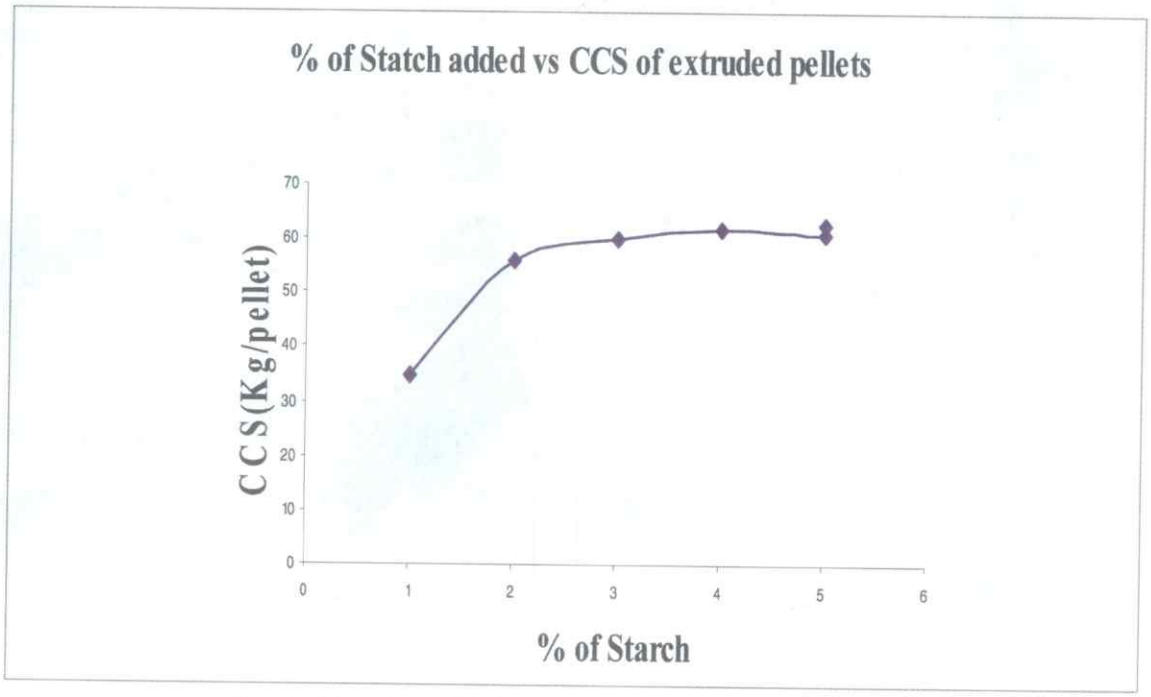


Fig. 4: Starch vs CCS of extruded pellets of blend-J

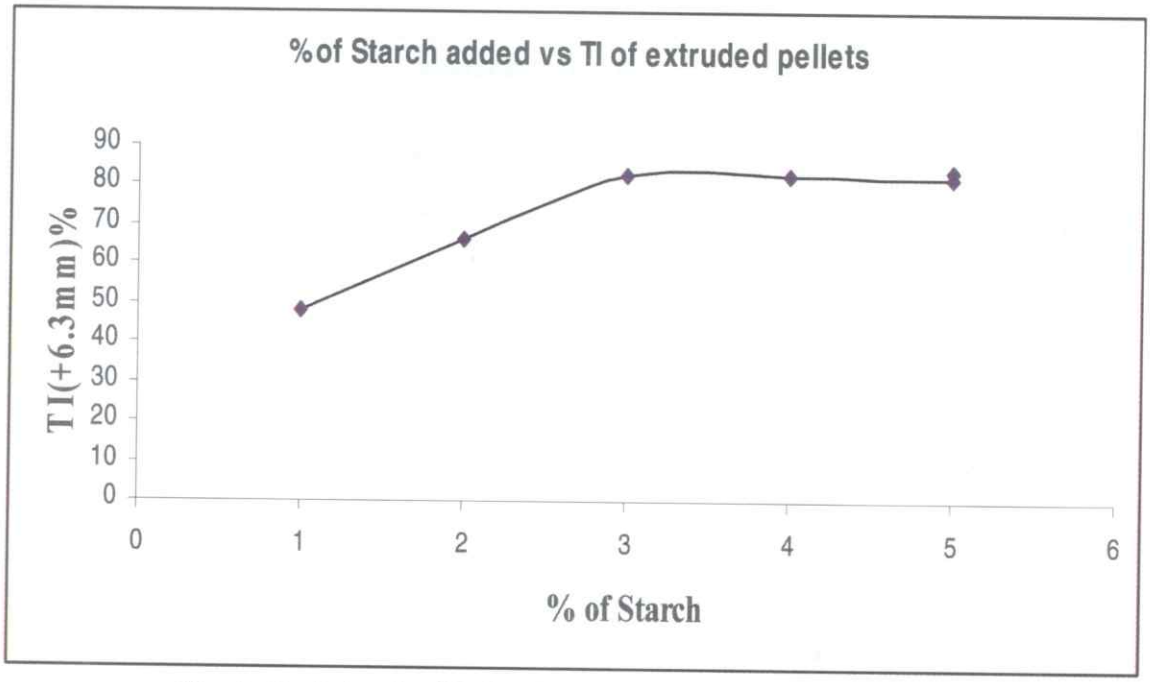


Fig. 5: % of starch added vs TI of extrude pellets of blend-J

a) Before Curing

b) After Curing

Fig. 6: Extruded agglomerates before and after curing

Table 4: Properties of Extruded Agglomerates

Chemical Analysis	
Fe(t), %	67
SiO_2, %	1.7
Al_2O_3, %	0.9
Physical Properties	
Tumbler Index (+6.3mm), %	83
CCS, kg/pellet	60
Porosity, %	31

Table 4 shows the chemical and physical properties of extruded agglomerates prepared with 3% Starch as binder.

CONCLUSIONS

1. Metallurgical wastes such as mill scale, CRM Oxide, BOF sludge etc. can be used in as received wet condition. Conventional agglomeration requires iron bearing material to be dried to the moisture level of 9 to 10 % for agglomeration.

2. The laboratory scale trials were encouraging. The CCS and TI (+6.3mm)% were found ~60 kg/pellet and ~83% respectively by using 3% starch as a binder by using blend-J.

3. Use of CRM oxide is not giving desirable CCS and TI for extruded pellets.

4. Further studies needs to be carried out to produce DRI using extruded pellets in RHF to make the usage in iron and steel making units.

REFERENCES

1. *Bogdan, Eugene A.; Cole, Richard L.; United States Patent 5395441*
2. *Lotosh, V.E. Steel USSR, (1973); 450*
3. *E.Hoffken, Stahl Eisen (1998); 108 (14-15), 51*
4. *Maneesh Singh: Doctoral Thesis, 2002:50, Lulea University of Technology, Sweden.*

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BIOLOGICAL EXTRACTION OF NICKEL: A VALUE ADDED METAL FROM CHROMITE OVERBURDEN

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ABSTRACT

Great concern exists for the management of large quantities of overburden generated by opencast chromite mining in Sukinda Valley, Odisha. Chromite overburden (COB) has been reported to contain low-grade nickeliferous laterite which requires a suitable technology to extract the value added metal. Bioleaching methods using indigenous micro-organisms have gained focus for nickel extraction as the hydrometallurgical and pyrometallurgical methods are energy consuming and cost intensive. Nickel is well-associated with the ferric form of iron present in the laterite which results in less recovery by nominal process. Dissimilatory iron reducing bacteria (DIRB) reduce the ferric content of COB, eventually causing a phase change and exposing the nickel for higher recovery. Pre-treatment of COB with DIRB consortia has been studied followed by acid leaching for enhanced nickel recovery. Acid-digestion of COB revealed the presence of 1% nickel. In XRD study, goethite and hematite peaks were observed in untreated ore while DIRB-treated ore showed magnetite peaks in addition to goethite and hematite peaks which confirm the reduction of iron. FESEM images show the variance of morphology from needle shaped goethite in original ore to granular magnetite in treated ore. Acid-wash of treated ore recovered 27% nickel which was enhanced to 69% on acid-leaching of treated ore. Hence, treatment of COB with DIRB can enhance the recovery of nickel.

Keywords: *Chromite Overburden, Dissimilatory iron reducing bacteria, bioleaching.*

INTRODUCTION

The discovery of metals by man is the building block of civilization. With time, the metals readily available on earth's surface got depleted, which led to deep excavations into the earth's crust to obtain the metals resulting in the formation of mines. 16.92% of the total mineral reserves of India are found in Odisha. Indian Bureau of Mines has provided the statistics of 12 different minerals reserves in various regions across the state. Chromite is the major reserve having near monopoly in the country found in the region of Keonjhar and Jajpur. Nickel is the next major reserve found in the same region existing as laterite ore in the chromite overburden.

Though nickel has notable metallurgical application, it has not been exploited significantly due to unavailability of suitable technology for efficient extraction. Nickel occurs in laterite form as the overburden of chromite opencast mines. Every year around 6 million tons of overburden seems to be generated [1] in addition to 140 million tons accumulated in the previous years. These dumps of chromite overburden hinder the lateral quarry development and are of major environment concern as the mining companies are not liable to grow trees in hope of developing a suitable technology for nickel extraction [2].

A step-change in the leaching process using microbes has the potential to offer better metal extraction methods. Microbial leaching of laterite ore has been studied using various micro-organiss like fungi [3,4,5], chemolithotrophic organisms [6,7,8]. Dissimilatory iron reducing bacteria (DIRB) is known to play a significant role in metal reduction and iron biomineralization [9,10] utilizing Fe (III) as terminal electron acceptor and organic matter as electron donor [11, 12] in natural subsurface environments. DIRB respire oxidized Fe (III), from ferric containing ore like ferric oxyhydroxide [9] and release Fe (II) which precipitate in the form of magnetite, siderite, vivianite under facultative anaerobic condition [12].

In this study, COB was treated with isolated iron reducing bacterial consortia to facilitate the iron reduction to bring about a phase change eventually releasing the ingrained nickel of goethite phase.

MATERIALS AND METHODS

Analysis of COB

The chromite overburden (COB) was supplied by Odisha Mining Corporation (OMC) from the ultramafic belt of Sukinda Valley in Jajpur, Odisha. The ore was crushed using mortar and pestle and sieved using a BSS mesh to obtain an average particle size of ~53μm for leaching studies. Mineralogical analysis of the COB sample was done using synchrotron XRD. The elemental analysis as shown in Table 1 was carried out using Atomic absorption spectrophotometer (AAS) after acid digestion of the ore.

Table [1]: Elemental composition of chromite overburden (COB)

Element	Ni	Co	Fe	Mn	Cr
%	0.9-1	0.09-0.1	40.52	0.61	2.6

Ni-Nickel, Co-Cobalt, Fe-Iron, Mn-Manganese, Cr-Chromium, Al-Aluminium
Values are mean of triplicate experiments

Sample Collection and Microbial Enrichment

Soil sample was collected from a depth of 3-4 cm from the bank of a stagnant, marshy pond (Sample designated as P1), and bank of a waste water drain (AV1, AV2) in vials, filled with water and was covered with air-tight enclosures.

Mineral salt media for facultative anaerobic growth of dissimilatory iron reducing bacteria (DIRB) was prepared by method of *Sungwan Kanso et al.*,(2002) [13] with the following modifications; Composition (g/L): KH_2PO_4-0.8; K_2HPO_4-3.0; KCl-0.2; NH_4Cl-1.0; $MgCl_2$-0.2; $CaCl_2$-0.1; Yeast Extract-0.05.The initial pH was 7.2. Glucose (10mM) as the sole electron donor and COB, Fe (III) source (2% w/v) as electron acceptor was added to the media in 100ml volumetric flasks. The media was autoclaved at 121°C for 20 minutes.

The sterile flasks were incubated with 1% (v/v) inoculum, layered with paraffin oil to maintain anaerobic condition and kept in dark for 7 days at room temperature. Enrichment was done by 5 consecutive transfers of inoculum to fresh media. The 5^{th} enrichment culture was used as inoculum for the bioleaching experiments to avoid discrepancies in the physiology of bacterial cultures. [14, 15]

Bioleaching by *In situ* Iron Reduction

The bioleaching experiment was carried out in 250ml volumetric flasks containing media with 1% (v/v) enriched inoculum of DIRB consortia and 2% (w/v) pulp density of ore for several days. Glucose, the electron donor (carbon source) was added every other day with shaking to ensure distribution of bacteria and iron minerals in the media. Every 7 days the culture was harvested through filter paper with mild-acid wash of the ore using 0.1N HCl. The liquor was analysed for the reduction of Fe (III) to Fe (II) by the estimation of ferrous content and total iron content by titration method as described by Vogel [16]. Nickel and Cobalt extracted was analysed using AAS. The treated ore was air-dried and analysed using synchrotron XRD.

The consortium with higher iron reducing capacity was inoculated for 25 days with pulp density 3% (v/v) COB. The treated ore was subjected to various concentrations of 1M, 4M, and 8M sulphuric acid for different durations with original ore as control. The leached liquor was analysed for the iron, nickel and cobalt content using AAS.

RESULTS AND DISCUSSION

Potential of Dissimilatory Iron Reducing Bacteria

The 3 enriched consortia showed a varied range of Fe (III) reduction as shown in Fig. 1. The highest bio-reduction of iron was observed in P1 consortia. The consortia were found to be gram-negative on gram staining.

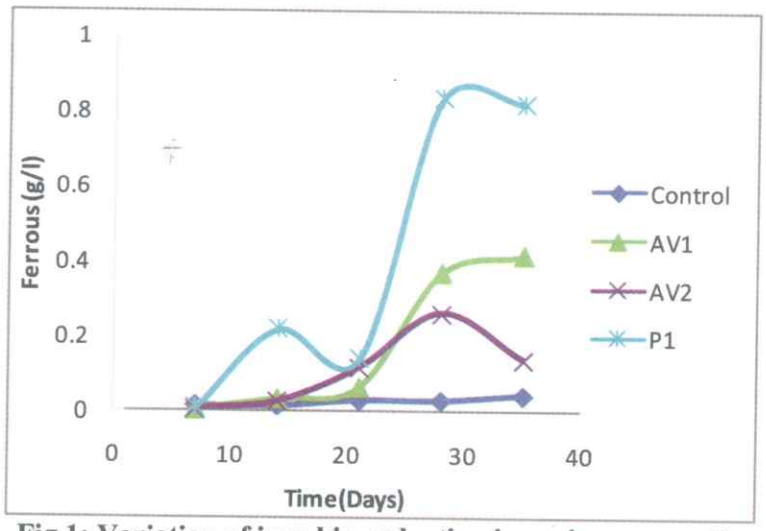

Fig 1: Variation of iron bio-reduction in various consortia

Influence of Bio-reduction of Iron on Ni Extraction

The kinetics of Ni and Co extracted during bio-reduction in P1 consortia is depicted in Fig. 2. It was observed that the Ni and Co extraction is proportional to the bio-reduction with 50% nickel recovery on acid-wash of the treated ore. This suggests that bio-reduction of iron directly influences the release of nickel associated within the Fe (III) matrix.

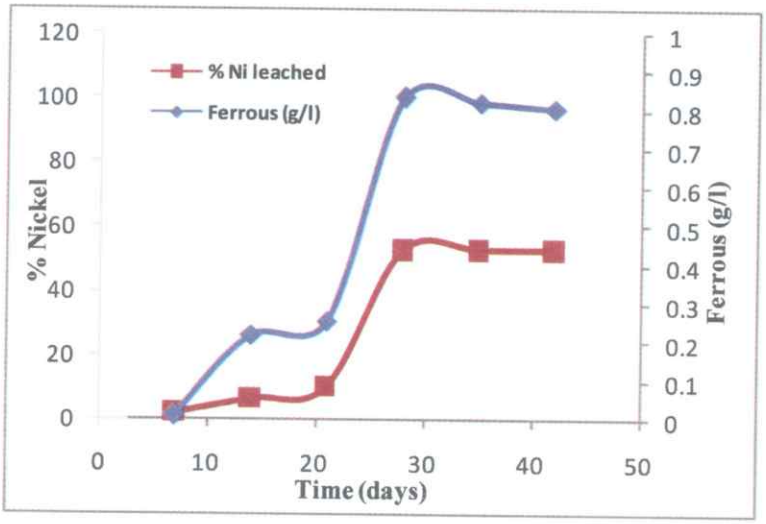

Fig 2: Bio-reduction dependent nickel extraction

Acid Leaching of Treated Ore

Acid leaching is essential for dissolution of nickel from treated ore. 27% nickel was obtained on leaching with 4M sulphuric acid for 2 days with the original ore which was enhanced to 69% on DIRB treated ore [Fig 3].

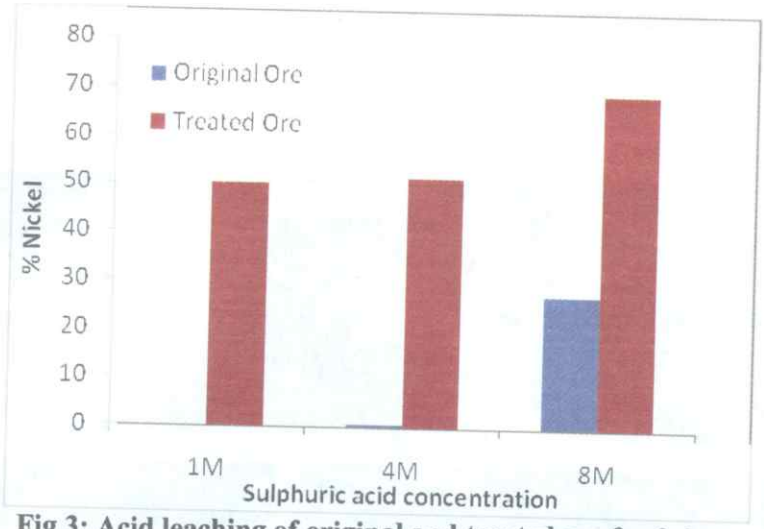

Fig 3: Acid leaching of original and treated ore for 2 days

Mineralogical Analysis of Treated Ore

Goethite, the major phase of laterite ore is a hydrated iron oxide [17]. Nickel is reported to be constrained in this goethite lattice requiring a phase change or dehydroxylation of this phase to liberate the nickel for easy accessibility and dissolution in leaching media.[17,18]

Fig. 3 shows the XRD pattern depicting the mineralogical characteristic change acquired by bio-reduction of iron using DIRB. The crystalline Ni phase appears in the treated ore along with magnetite peaks. This observation confirms the physical and mineralogical change resulting in the liberation of Ni due to bio-reduction.

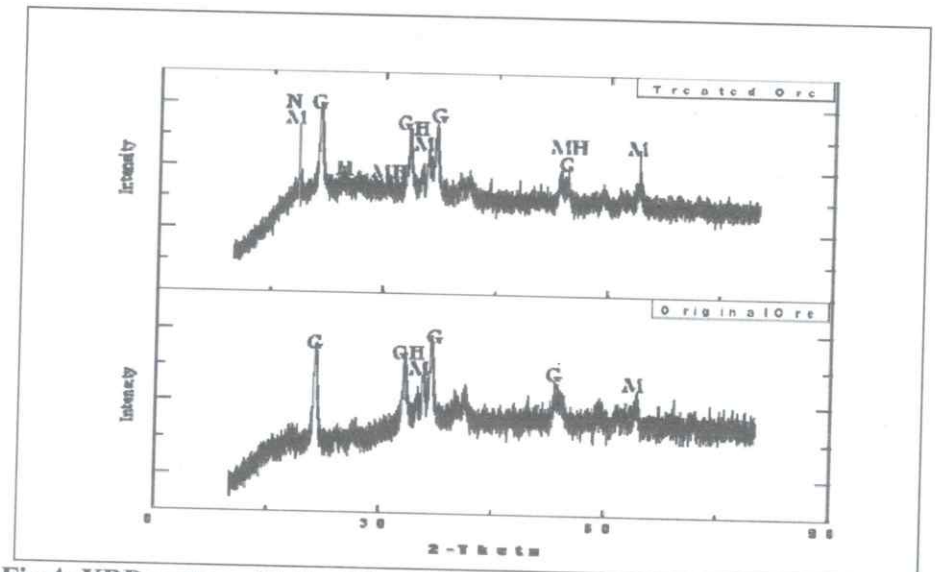

Fig 4: XRD pattern (G-Goethite, M-Magnetite, H-Hematite, MH-Maghemite, N-Nickel oxide)

The morphological transformation subsequent to the mineralogical change was observed under FESEM. Fig. 4 clearly exemplifies the presence of needle shaped goethite in the original ore and the loom of nano-sized grains identified as magnetite was observed in the DIRB treated ore in agreement with the description given by Hansel [19]. The mistiness observed in the treated ore reveals that iron reducing bacteria associate with the ore by biofilm formation.

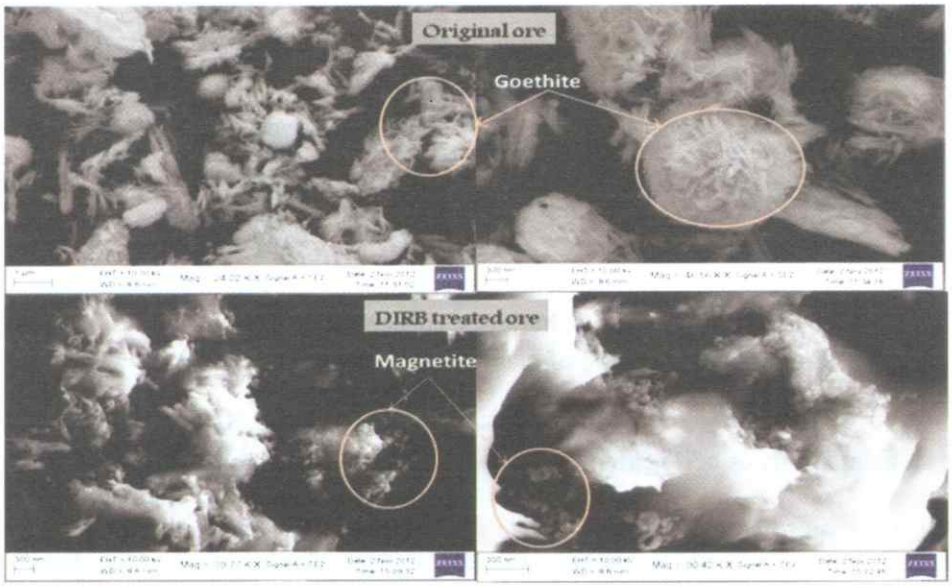

Fig 5: Original ore-needle shaped goethite; DIRB treated ore: granular magnetite

CONCLUSION

This work demonstrates that the bio-reduction of iron assisted the release of captivated nickel from the goethite of COB. The XRD analysis of original COB and reduced ore reveals the phase change from goethite to magnetite and hematite exposing the nickel content which is confirmed by the morphological study. Nano-sized grains of magnetite were observed along with needle shaped goethite of goethite ore in FESEM. The biofilm observed confirms the close microbe-mineral association essential for iron reduction of the COB. Enhanced Nickel recovery of 69 % was observed on bio-reduction using DIRB whereas only 27% nickel was obtained with original ore. Pre-treatment by bio-reduction of ore can enhance the potential of nickel extraction forecasting an efficient method of nickel extraction in the field of metallurgy.

REFERENCES

1. *Swain, P.K., Gautam Roy, Chaudhury and Sukla, L.B. (2007). Korean J. Chem. Eng., 24(6), p. 932.*
2. *Rama Murthy, Y. Chenna Rao, B. Gajanan Kapure, Vilas Tathavadkar. (2010) New prospective For the Utilisation of Indian Lateritic Chromite Overburden Proceedings of the XI International Seminar on Mineral Processing Technology (MPT-2010) pp. 158–165.*
3. *Bazgha Ahmad, Haq Nawaz Bhatti and Sadia Ilyas. (2011)Bio-extraction of metal ions from laterite ore by Penicillium chrysogenum. African Journal of Biotechnology Vol. 10(54), pp. 11196-11205.*
4. *Sunil Kumar Behera, Prangya Parimita Panda and Lala Behari Sukla. (2011) Microbial Recovery of Nickel and Cobalt from Pre-treated Chromite Overburdens of Sukinda*

Mines using Aspergillus niger. Recent Research in Science and Technology, 3(6): 28-33

5. *Le, L., Tang, J.A., Ryan, D., Valix, M., 2006. Bioleaching nickel laterite ores using multimetal tolerant Aspergillus foetidus organism. Minerals Engineering 19, 1259–1265.*
6. *Rawlings, D.E., (2005). Characteristics and adaptability of iron- and sulphur-oxidising microorganisms used for the recovery of metals from minerals and their concentrates. Microbial Cell Factories 4, 13.*
7. *Simate, G.S., Ndl vu, S., Gericke, M., (2009a). The effect of elemental sulphur and pyrite on the leaching of nickel laterites using chemolithotrophic bacteria. Hydrometallurgy Conference 2009: The Southern African Institute of Mining and Metallurgy.*
8. *Simate, G.S., Ndlovu, S., Gericke, M., (2009b). Bacterial leaching of nickel laterites using chemolithotrophic microorganisms: process optimisation using response surface methodology and central composite rotatable design. Hydrometallurgy 98,241–246.*
9. *Richard B. Frankel, Dennis A. Bazylinski. (2003) Biologically Induced Mineralization by Bacteria. Reviews in Mineralogy and Geochemistry54(1) pp. 95-114*
10. *Yul Roh, Haichun Gao, Hojatollah Vali, David W. Kennedy, Zamin K. Yang, Weimin Gao, Alice C. Dohnalkova, Raymond D. Stapleton, Ji-Won Moon, Tommy J. Phelps, James K. Fredrickson, and Jizhong Zhou. (2006) Metal Reduction and Iron Biomineralization by a Psychrotolerant Fe(III)-Reducing Bacterium, Shewanella sp. Strain PV-4 Applied And Environmental Microbiology, , p. 3236–3244 Vol. 72, No. 5*
11. *Lovley DR (1990) Magnetite formation during microbial dissimilatory iron reduction. In: Iron Biominerals. Frankel RB, Blakemore RP (eds) Plenum Press, New York, p 151-166*
12. *Lovley DR (1991) Dissimilatory Fe(III) and Mn(IV) reduction. Microbiol Rev 55:259-287*
13. *Sungwan Kanso, Anthony Greene, C. Bharat. Patel, K. C. (2002) Bacillus subterraneus sp. nov., an iron- and manganese-reducing bacterium from a deep subsurface Australian thermal aquifer. International Journal of Systematic and Evolutionary Microbiology, 52, 869–874*
14. *C. García-Balboa1, a, D. Cautivo2, b, M. L. Blázquez1, c, F. González1, d, J. A.Muñoz1, e and A. Ballester. (2009)The influence of disimilatory Fe(III) reducers on iron ore dissolution Advanced Materials Research Vols. 71-73 pp 501-504*
15. *Y. Li, H. Vali, J. Yang, T.J. Phelps and C. Zhang (2006): Geomicrobiology Journal Vol. 23 p.103*
16. *Vogel: Textbook of Inorganic Analysis: 4th Ed. P 348-351,370-372*
17. *Smaranika Mohapatra, Chandan Sengupta, Bansi Dhar Nayak, Lala Bihari Sukla, and Barada Kanta Mishra (2009)Biological leaching of nickel and cobalt from lateritic nickel ore of Sukinda mines Korean J. Chem. Eng., 26(1), 108-114*
18. *Valix M., Tang J.Y. and Cheung W.H. (2001). The Effects of Mineralogy On The Biological Leaching Of Nickel Laterite Ores Minerals Engineering, Vol. 14, No. 12, Pp. 1629-1635.*
19. *Hansel C.M., 2004, PhD Thesis: Bacterial and geochemical controls on the reductive dissolution and secondary mineralization of iron (hydr)oxides. Department of geological and environmental sciences, Stanford University.*

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SONIC TECHNOLOGY FOR REMOVAL OF CHEMICAL CONTAMINANTS FROM SOIL ON A LARGE SCALE

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ABSTRACT

Power ultrasound can be used for the rehabilitation of industrial sites or the reclamation of polluted land by the removal of chemical and biological contamination from soil. Earlier applications of sonic energy involved the use of ultrasound, in which the frequencies are very high; however, ultrasound has proven difficult to apply to large scale-processes due to the low energy transfer from typical transducer technologies. Through ore leaching and cleaning studies the authors' group have demonstrated the benefits of sonic energy are not limited to ultrasound frequencies, and sonic technology based on a high-energy, low-audio-frequency sonic generator has therefore been developed. Sonication improves the desired physical, chemical or biological processes by an order of magnitude (10X) over conventional processes. The environmental sonoprocess uses sonic energy in both the extraction and chemical destruction of polychlorinated bi-phenyls (PCBs) in contaminated soil. PCBs are extracted from the soil into a solvent, leaving the soil free of PCB. The sonoprocess then chemically destroys the PCBs via sodium-based dechlorination. The PCB sonoprocess plant developed in modules elsewhere was based on the authors' basic results with an added advantage of allowing the system to be deployed on site. Several benefits can be derived by the use of sonic technology viz., eliminates the need to transport PCB-contaminated soil, and it is also non-thermal, avoiding the risk of high-temperature air emissions. This presentation describes the sonoprocess technology with typical results and commercial operating practices.

1. INTRODUCTION

Most of the developed as well as developing world these days are aware of the problems caused by soil pollution. Gone are the days when waste could simply be buried and forgotten. Legislation is becoming tougher and so methods of both preventing and curing pollution are receiving a great deal of attention. Soil that is contaminated with chemical presents a range of problems to the environment **[1]**. These can include the destruction of ecosystems a loss in agricultural productivity, contamination of water resources and human and animal illness through direct ingestion of dust and the consumption of foods which have grown on contaminated land. The chemical pollution itself can arise from a number of sources e.g.fall-out from incinerators or nuclear plants, residual pollution from industrial sites on the retention of herbicides or insecticides used in agriculture.

In land remediation, for contaminated soil wastes the currently available options for management and disposal **[2]** are principally (i) permanent storage in a secure landfill. This will result in a permanent retained liability by the waste generator, (ii) incineration in a permitted waste incinerator. This is costly and entails the risk of atmospheric emissions and (iii) soil washing to produce bulk soil with low-level contamination. However the washing process itself will produce a volume of solvent that must be treated before disposal.

There are two ways in which acoustic energy can enhance soil washing. These are predominantly mechanical and involve a combination of abrasion to remove superficial impurities and improved solvent leaching of contaminants from the interior of particles. Present authors' group investigated leaching of metals from ores using ultrasound **[3-7]** as well conducted studies on ash removal from coal **[8]** coal washing **[9]** and removal of iron from reduced ilmenite **[10]** and. For the first time, in the year 2001, we reported **[4]** that peak metal extraction/leaching values can be realized by sonic reactors at ~audible frequencies [200 Hz]. It also addresses the large scale problems useful in industrial/commercial scale. This paper presents details of a sonic device that was

developed by a Canadian firm in 2005 based on the science content reported by us. It is used for both the extraction and chemical destruction of polychlorinated bi-phenyls (PCBs) in contaminated soil in a large scale especially used for onsite treatment.

2. DEVELOPMENT OF A SONIC DEVICE FOR SOIL DECONTAMINATION

For chemical decontamination of soils two basic mechanisms for acoustically enhanced soil cleaning have been envisaged. (a) An improvement in leaching out more deeply entrenched materials and (b) an increase in the abrasion of suspended soil in slurries leading to the removal of contaminated material from the surface of particles.

2.1(a). Leaching mechanism:

Any improvements in the penetration of solvent into particulate matter will result in the enhanced removal of soluble material that may be trapped inside the solid particles. This process is referred to as ultrasonic leaching and has been investigated for the decontamination of different types of soils e.g. landfills, mining spills and river sediments, batch tests for accelerating leaching have used ultrasound for the removal of radio nucleotides and heavy metals from soils [11]. The application of ultrasound has also been found to aid precious metal recovery from waste production including industrial, municipal and mine wastes [12].

Although there is plenty of experimental evidence that ultrasound improves leaching the exact mechanism is not fully understood. The present authors' have suggested models for leaching in the absence and presence of ultrasound [6], as shown in fig.1. Normal leaching takes place as the solvent front moves inward and steady state diffusion occurs through the depleted outer region and is equal to the rate of reaction within the reaction zone itself.

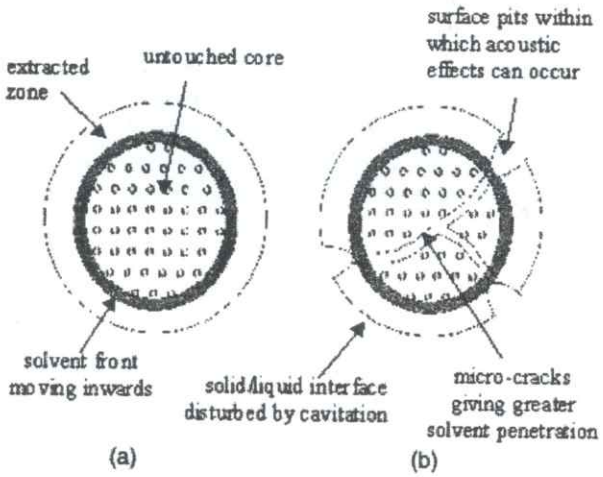

Fig.1. Leaching of contaminants from soil particles (a) normal leaching (b) in the presence of ultrasound.

There are some parallels and differences between the use of audible sound frequencies for leaching/cleaning and the use of ultrasound frequencies. Due to the variation in generation of number of cavitational events and intensities, perhaps it is not unexpected if we extrapolate back from I MHz through the lower generation at 20 kHz and then down to audible. Studies conducted by the present investigators on peak metal extraction values (in per cent) from ores as a function of frequency (as shown in fig.2) revealed that optimum leaching is attainable at 200 Hz frequency.

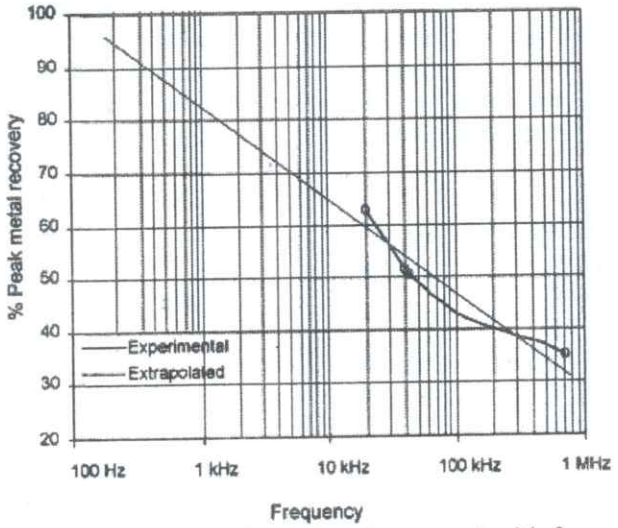

Fig.2. Peak metal extraction values in per cent with frequency

2.2(a). Role of audible frequency in soil cleaning:

Soil pollution can occur through a variety of causes and the search for methods for removing it is actively pursued. A wide range of technologies is available but the main processes developed upon washing out the contamination, using bacteria to digest it, producing an impenetrable barrier to stop contaminant migration and heating. Of these options washing is the most attractive but it suffers from one difficulty - the production of large volumes of contaminated solvent rather than soil [e.g. coal cleaning for ash reduction, ref **9**].

2.2(b). Frequency versus application:

Frequency impacts the diameter of the cavitation event. Low frequencies result in large diameter cavitations and higher frequencies result in small diameter cavitations. The energy per cavitation follows the same trend. However, the number of cavitations per unit volume is high with high frequency systems and low with low frequency systems. The combination of energy per cavitation and number of cavitations is total energy and this is equal for both frequencies as displayed in fig.3. Because of this relationship, 40 kHz is generally considered the precision cleaning frequency, dominating most cleaning applications. Low frequency systems have done well in high mass applications where the soil to be removed is extremely difficult, but complete removal is not required, such as removal of sand after aluminum casting in sand forms.

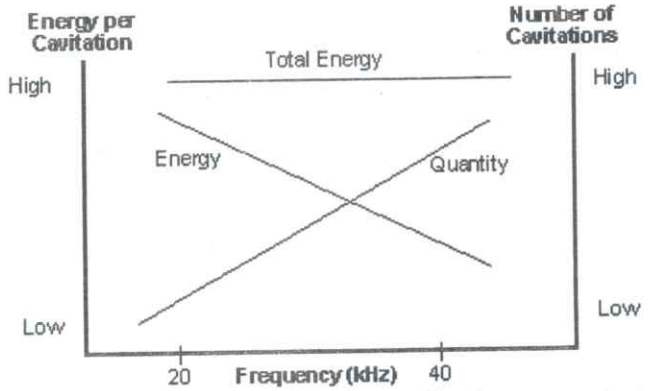

Fig.3. Frequency versus cleaning application parameters.

Cleaning by the interaction of sound with liquid—sonics, ultrasonics and megasonics—is an ongoing source of inspiration and controversy. Sonics, ultrasonics and megasonics are not distinct or competing techniques but are actually a continuum. All three are based on sound waves traveling through liquid, producing cycles of compression and rarefaction. Vapor-filled bubbles result from tears in the liquid. The differences between them are in the frequencies of these sound waves. At lower ultrasonic frequencies, cavitation bubbles (actually vacuum voids) are relatively transient, growing then imploding with tremendous localized force and heat. At the higher frequencies associated with megasonic cleaning, bubbles are smaller and more stable.

At a given frequency, the power defines the cavitation threshold, above a certain power; cavitation happens, underneath, there is only the spreading of the waves in a environment. Therefore, underneath this cavitation threshold, we are in an area where ultrasounds only create wave movements within an environment. [p187 in **ref 7**]. We investigated effect of frequency with regards to cavitation by the use of a typical aluminium foil tests conducted in two different ultrasonic baths. Results are displayed in fig. 4, showing low frequencies (20 kHz) have profound cavitation effect than high frequencies (40 kHz) as seen by pits and holes in alumiminum foil.

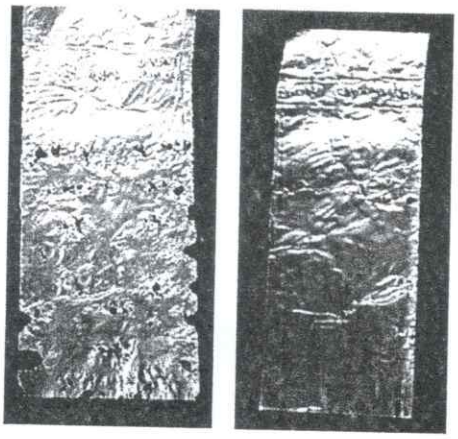

Fig.4. Effect of frequencies on aluminium foil, result obtained after 10 min in a ultrasound tank, left 20 kHz, right 40 kHz freq.

This observation is significant and has recently been confirmed by Australian researchers by investing the effect of ultrasound on the conventional mechanical soil-washing process **[13]**. They conducted tests with aluminum foils under four frequencies including 35, 72, 110, and 170 kHz. It is known that the physical effects generated during acoustic cavitation damage the foil by causing pits and holes. The sonication at 35 kHz resulted in maximum damage to the aluminum foil as compared to that observed at other frequencies. Extrapolation of this result also lead to lower audible frequencies has profound influence on cleaning process. The efficiency of washing in (i) diesel removal efficiency, (ii) process time, (iii) consumption of electric energy, and (iv) production of washing leachate under ultrasonic processing conditions was similar to that observed with mechanical washing and also suggests further that the ultrasonic washing process does not require external chemicals like sodium dodecyl sulfate (SDS) and can be considered as a "green" process. The present authors' study on Al foil test was well supported by other workers **[13]** advocating for very low audio frequency transducers are useful for soil cleaning.

Australia suffers from soil pollution as do many developed countries and researchers

of New South Wales have begun a project in which ultrasound is used to enhance the rate of clean-up of soils **[14]**. Laboratory studies have been made for the removal of various contaminants like insecticides and polycyclic aromatic compounds using 12.5 mm tip diameter sonotrode [horn] delivering approximately 170 W. The studies later extended to the decontamination of a river sediment. This was an industrial site polluted with polycyclic aromatic hydrocarbons (PAHs) compounds (containing at least 15 compounds). The sediment with an original contamination of approximately 400 ppm, was made upto 44.4 wt.% with distilled water and then sonicated above with a 4 kW ultrasonic system. Basically the method suffers from a serious hurdle that probe tip is being eroded limiting versatility of the method for large scale applications. An example of probe erosion is shown in fig.5. Tests for prolonged operation were carried out by one of the author (KMS) in TUHH, Germany during 1998 revealed that pitting occurs at sono-probe surface warranting probe replacements for any further experimentation.

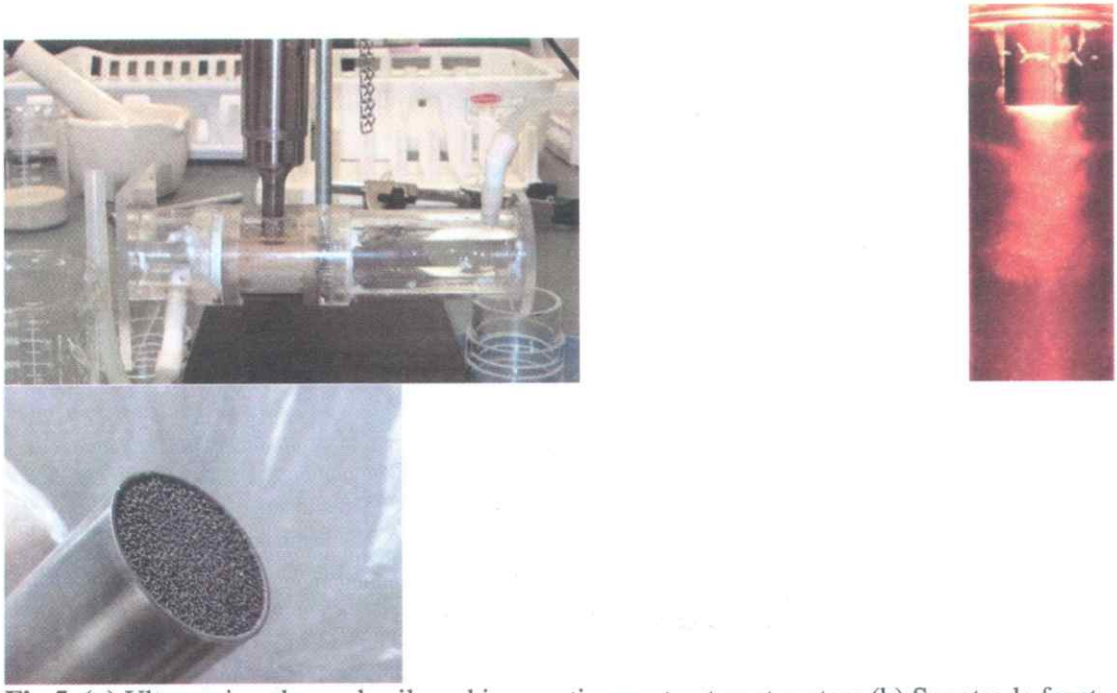

Fig.5. (a) Ultrasonic enhanced soil washing continuous treatment system (b) Sonotrode front - emitting surface - erosion caused by intensive cavitation and sonication; (c) After 3 months of operation: 1000 watts, 20 kHz

To reduce 70% destruction of pesticide an estimate of the cost of scale-up treatment showed that one need 125 kWh of power per tonne of soil, based on treatment of 200 g 10 min at 150 W DDT-contaminated soil. Now, this does not represent very much power/cost compared with other technologies. So, hitherto ultrasonic probe method is not versatile due to two drawbacks; severe tip erosion and high costs involvement.

Altogether a different approach was attempted in USA during 1998 **[15]** to detoxify volatile organic contaminated soil by pneumatic whistle transducers generating 5 kHz frequency. The in-situ field pilot tests coupling sonic whistles and soil fracturing shown to reduce an initial contaminant weight of eleven pounds in the bed to one pound was reduced by a factor of at least 7 with the whistle. The whistle, in particular, has demonstrated a contaminant mass removal rate of 1000 percent more than the control and the time required. These studies will provide the "leap" from bench scale to field scale which is a crucial step in technology development, training, and transfer. But it has two limitations; i)

transfer acoustic energy in to soil is far less due to large acoustic impedance difference, and ii) tight bedrock is more difficult due to the characteristics of low permeability and high adsorption potential of these geologic materials.

It is evident from the above that neither sonotrode (sonic probe) nor whistle (acoustic air-jet generator) could cater for large scale soil decontamination application. Hence present authors suggest a new type transducer can work at low audible frequency should be developed and evaluated, other than sonotrode or pneumatic whistle.

2.3. Examination of sonic process methodology

In general, at low frequencies (20-30 kHz), a relatively smaller number of cavitations with larger sizes and more energy are generated. As mentioned above, at higher frequencies, much denser cavitations with moderate or lower energies are formed (Fig.6). Low frequencies are more appropriate for cleaning heavy and large-size components, while high frequency (60-80 kHz) ultrasonics is recommended for cleaning delicate surfaces and for the rinsing step.

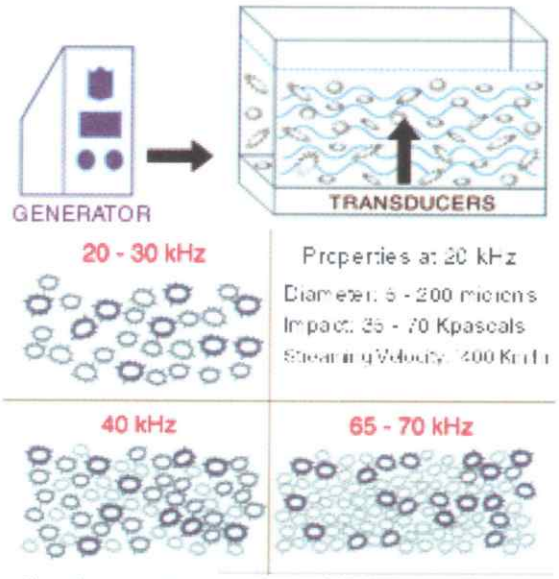

Fig. 6 (a). Ultrasonic cleaning system. **6 (b)** ultrasonic frequency and cavitation.

Estimates of cavitation abundance at various ultrasonic frequencies have shown that the number of cavitation sites is directly proportional to the ultrasonic frequency. For example, about 60 to 70 percent more cavitation sites per unit volume of liquid are generated at 68 kHz than at 40 kHz. The average size of cavities is inversely proportional to the ultrasonic frequency. Therefore, one would expect that at the higher frequency, at a given energy level, the scrubbing intensity would be milder, particularly on soft and thin or delicate surfaces, and more penetration and surface coverage into the recessed areas and small blind holes would be expected.

The energy released from an implosion in close vicinity to the surface collides with and fragments or disintegrates the contaminants, allowing the detergent or the cleaning solvent to displace it at a very fast rate. The implosion also produces dynamic pressure waves which carry the fragments away from the surface. The implosion is also accompanied by high speed micro streaming currents of the liquid molecules **[16]**.

The cumulative effect of millions of continuous tiny implosions in a liquid medium is what provides the necessary mechanical energy to break physically bonded contaminants, speed up the hydrolysis of chemically bonded ones and enhance the solublization of ionic

contaminants. Extrapolation of the above facts to very low frequencies ~ 200 Hz advocates in speeding the removal rate of various contaminants while the chemical composition of the medium is an important factor

Thus, the present author established in 2001 the science behind the application of audible frequency sonics in enhancement of leaching process [4] and also established that at low sonic frequency improves the washing/cleaning of soils in a large scale. Further, there exists a need to develop new transducer which different from existing sonotrode or a pneumatic whistle like for e.g. electromagnetic vibrating rod transducer. These suggestions have implications in proposing an onsite technology development, eliminating the need to transport hazardous materials through populated communities. The above result has laid foundation and lead to the development of a sonic device. So engineers from Sonic Environmental Solutions Inc, Canada later (in 2005) have developed a sonic device whose description along with typical results is given in the foregoing section 3.

3. THE LOW FREQUENCY SONIC DEVICE

Sonic device produces audible acoustic energy for large scale processing. This involves generated vibrational energy through the use of resonant bending modes in a large cylindrical steel bar [17]. The bar is driven into a clover leaf type of motion by firing three powerful electromagnets in sequence which are located at each end of the bar. The bar is supported by air springs so that the ends and the centre are then caused to rotate at a resonance frequency depending on its size (fig.7). One such unit, operating at a power of 75 kW, drives a bar that is 4.1 m long and 34 cm in diameter at its resonance frequency of 100 Hz. The bar itself weighs 3 ton and produces a vibrational amplitude at each end of 6 mm – considerably larger than the amplitudes available through sonochemical processing and hence better for the dispersal of materials in liquids.

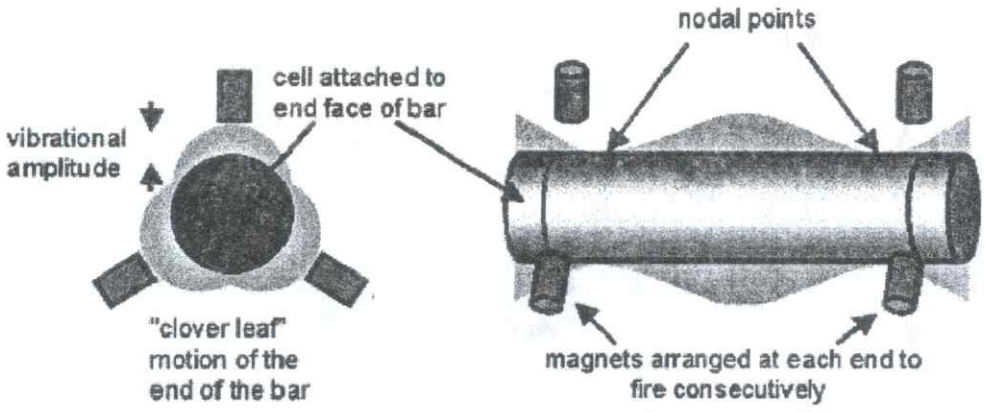

Fig.7. Vibrating bar system

4.1 Description of the Pcb-Soil Treatment Sonoprocess Technology

The principal unit operations of Sonics PCB soil treatment process based on sonic technology are (i) Soil excavation, sorting and sizing, (ii) Mixing of sized soil with hydrocarbon solvent (iii) Heating the soil-hydrocarbon slurry to 105-110^{0}C (iv) Pumped circulation of the slurry through the sonic mixing chamber to facilitate de-agglomeration of soil and extraction of PCB (v) Addition of sodium (ingot) to process slurry (vi) Sonic micro-dispersion of sodium by circulation of the process slurry and sodium metal through the sonic chamber (vii) Solvent recovery by decantation and froth flotation (viii) Soil dewatering and finally (ix) Solvent and process water are recycled.

For a batch testing (as shown in fig.8) sonoprocessing applications, mixing chambers are rigidly mounted on each end of the bar. Materials in the form of a liquid slurry can then be pumped through these chambers in order to perform operations such as mixing, grinding and the destruction of hazardous waste.

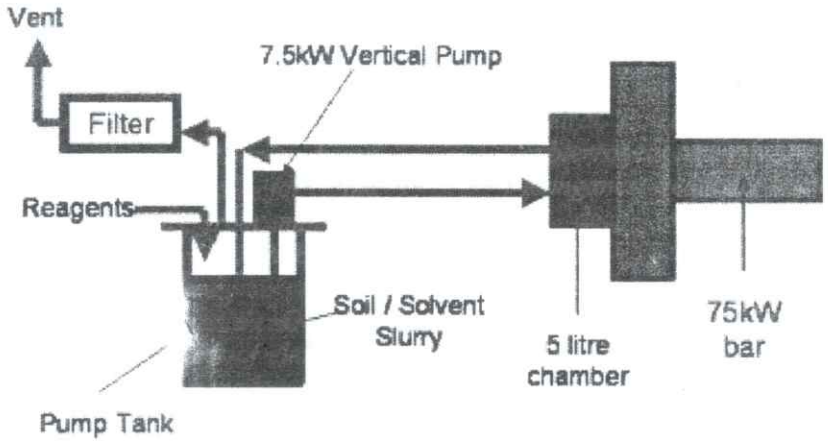

Fig.8. Pumped test on batch system.

For continuous mixing operations it is necessary to feed the discharge process fluids and so the connecting tube between the vibrating chamber and the rigid external piping system must be flexible, fatigue resistant and chemically inert to the materials being processed. The chambers used for any particular application will be process specific in terms of both residence time and the internal surface area and geometry. A process matrix slurry [combination of PCB contaminated soil (or sediments) and solvent] is pumped through the sonic chambers. PCB sonoprocess de-agglomerates the PCB in the soil, into the process matrix. Once the PCBs are suspended in the matrix, it is possible to chemically destroy them using a chemical reaction, again made possible by the sonic generator. Post sonication treatment includes conventional methods for separating the solvent from the soil and resulting end products are low grade fuel, salt and clean soil/sediment. When this technology is applied to PCB-contaminated soil, it produces clean soil (i.e. contains less than 2 ppm of PCB material). PCB sonoprocess is an ex situ, semi-continuous process and operates at low temperature without any possibility of creating adverse by-products such as chloro-dioxins or furans, which if present, are also destroyed. The sonoprocess solution provides permanent destruction of PCB, and does it on-site in a sustainable and cost-effective manner.

4.2. Soil decontamination mechanism in an ultrasonic field:

Ultrasonic waves traveling through the mixture create micro-bubbles. When these bubbles burst on the surface of the soil particles, they release intense shock waves which can generate temperatures of up to 5000 K. Any chemical contaminants on the surface of the soil particles bear the brunt of these bursts of energy and are blown apart. Each evaluation of ultrasonic cavitation acts as a localized 'hot spot' generally temperatures > 5000 K and pressures excess of 100 MPa the implosion happens with a collision density of 1.5 Kg cm^{-2} and pressure gradients of 2 TPa cm^{-1} with life times shorter than 0.1 μs; cooling rates above 10^{10} K s^{-1} are involved **[6]**. Importantly, the surrounding liquid stays cool, eliminating the possibility that the remnants of the toxic compounds can recombine to form dangerous by-products, as sometimes happens using other technologies. Dioxins

are formed during incineration, for instance.

Higher the operating temperature, lower is the residual contaminant concentration. Thus, suggesting that application of ultrasound result in temperature raise that could increase the detoxification rate of a soil/water mixture. The detoxification rate would be improved because cavitation raises temperature, resulting in increase the internal energy of adsorbed molecules; provide the required desorption energy, and make the adsorbed molecules more easily desorbed. In addition, a rise in temperature caused could increase the diffusion velocities of desorbed molecules and thus increase the desorption rate. Therefore, on the basis of the above information, the detoxification of contaminated soil can be made more efficient in presence of ultrasound **[18,19]**.

4.3. Treatment of non-metallic PCB material and PCB waste oils

For oils and similar concentrated PCB material the process involves destruction of the PCB through sodium reduction using sonic energy to create an efficient reaction. For soils there is a preliminary step involving de-agglomeration of the PCB soil with a solvent using sonic energy. Application of low frequency sonic energy to a solvent and soil slurry to create a sonoprocess which will allow the PCB to be de-agglomerated from the soil and subsequently a second sonoprocess is used to create an efficient reaction with the PCB and sodium. Byproducts produced by sonic technology are given in table-1.

Table-1. What byproducts does the technology produce?

Byproduct	Kind	Amount
Liquids	Low grade heating oil fuel Process Water	10 – 20 L per tonne of soil treated 10 -20 L per tonne of soil treated
Solids	Na (Salt)	1 Kg NaCl / Kg PCB
Air	Vent gas – mainly nitrogen	16 m^3 per tonnes of waste treated

4.4. Sonic device cost and treatment capacity:

One mobile unit costs approximately $2.5 million and can process 30 tonnes of PCB-contaminated soil in an eight-hour shift, or 90 tonnes if three eight-hour shifts are employed. As such, one unit can process between 7,500-22,500 tonnes of PCBcontaminated soil per year, based on 250 days of operation.

4.5. Treatment and disposal costs :

Using terra-kleen-treatability study of soil; 500, 1,000, and 10,000 Cu yards cost per ton calculated as 300, 210 and 170 USD respectively in 2005. The unit cost includes the estmates for remediation, site preparation, residuals, shipping, handling and disposal. Recent (in 2012) approximate costs for applying the technology per unit, including costs for all technical pretreatment steps, excluding all costs not related to the technical application of the technology (transport costs, costs for disposal of decontaminated transformers/ capacitors/materials, etc.). For (a) non metallic PCB materials (soil, sediment, sludge granular solids) 750/Tonne USD and for (b) transformer oils 750/Tonne USD.

5. MERITS AND DEMERITS OF THE DEVELOPED SONIC TECHNOLOGY

Sonoprocess – a worthy competitor to incineration: While other technologies can treat PCB-contaminated materials, incineration was listed as a "best demonstrated available technology" by the U.S. Environmental Protection Agency (U.S. EPA), and the most effective at the actual destruction of PCBs. Sonoprocess can also effectively achieve the same destruction capabilities, but without emitting any harmful emissions into the atmosphere. In addition, below is a quick

snapshot of the pros and cons of this particular sonic technology.

Advantages : (i) The unit is physically located on the contaminated site being mobile, which sharply reduces the cost and time required to transport soil for remediation.(ii) The unit can be deployed into remote areas or globally, if required (iii) The technology doesn't create hazardous by-products during the PCB destruction process. (iv) Soil can be recovered for re-use as backfill. (v) The unit has a smaller footprint and takes up less space. (vi) A new mobile unit can be built faster in three to four months.

Disadvantages: (i) Sonoprocess is a new technology and may take time to gain acceptance in the market place. (ii) It may not be cost effective if there is a competing technology such as incineration close to the contaminated site. (iii) The current mobile unit cannot process contaminated soil as quickly as an incineration plant.

6. SUMMARY AND CONCLUSIONS:

The decontamination of chemically contaminated soil presents numerous challenges. Many tasks are involved, each of which requires adherence to a complex array of federal and state regulations and policies, attention to health and safety issues for workers and the public, monitoring and the management of schedules and costs. And interaction with potential entrepreneurs who have interest in the present activities as well as future plans for site treatments.

The present authors' results formulated basis for developing a sonic technology for soil decontamination. We showed that acoustically enhanced soil cleaning can be achieved at audible frequency due to increase in the abrasion of suspended soil in slurries leading to the removal of contaminated material from the surface of particles and also through improvement in leaching out of more deeply entrenched materials as proposed by the leaching mechanism. Due to some limitations of sonotrode and pneumatic whistle we suggest a new type transducer based on electromagnetic that can work at low audible frequency should be developed and evaluated. Such a system can be deployed on-site soil decontamination. PCB destruction by sonoprocess offers the best available solution to PCB contaminated soils and PCBs in oils. The sonic technology deals with PCB problems onsite, eliminating the need to transport hazardous materials through populated communities. The developed technology is mobile solution and is non-thermal, eliminating unwanted by-products such as chloro-dioxins and furans.

Today's sonic transducers operatable at audio frequency are reliable, efficient devices which can be used with confidence in large scale applications. Arguments against the reliability of low sonic frequency transducers and in favor of ultrasonic transducers technology are based on historical information which is now out-dated and largely inaccurate. Sonic technology is a new and rapidly growing field of study, the applications of sound in green chemistry and environmental applications have a promising future. Compared to conventional methods, sonication can bring various benefits, such as environmental friendliness (no toxic chemicals are used or produced), cost efficiency, and compact, on-site treatment. Besides an overview of the sonic leaching and washing studies, this paper summarizes the main findings and innovations of recent equipment for large scale soil remediation. We propose a new comprehensive measure – Mine Prosperity Index (MPI) based on equitable development and environmental sustainability parameters along with productivity and infrastructure; quality of life should be formulated. Sonochemical land remediation is a route to lean, green and clean soil treatment.

REFERENCES

1. *Reena Amatya Shrestha, Tmy-Duong Pham and Mika Sillanpää, Ultrasound and Sonochemistry in the Treatment of Contaminated Soils by Persistent Organic Pollutants,*

Handbook on Applications of Ultrasound, Sonochemistry for Sustainability (Chapter 16), Edited by Ackmez Mudhoo, CRC Press 2011

2. *T.J.Mason, A. Collings, A. Sumel, Sonic and ultrasonic removal of chemical contaminants from soil in the laboratory and on a large scale, Ultrasonics Sonochemistry 11(2004), 205-210.*
3. *K.M.Swamy and K.L.Narayana, Ultrasound in Leaching in the Series of Advances in Sonochemistry, Volume 6, 2001, 141-180, Published by JAI Press, USA*
4. *K.M.Swamy and K.L.Narayana, Intensification of leaching process by dual-frequency ultrasound, Ultrasonics Sonochemistry, 8, (2001), 341-346*
5. *K.Sarveswara Rao, K.L.Narayana, K.M.Swamy and J.S.Murty, Influence of ultrasound in ammonical leaching of copper oxide ore, Metallurgical and Materials Transactions 28B, (1997) 721-723.*
6. *K.L.Narayana, K.M.Swamy, K.Sarveswara Rao and J.S.Murty, Leaching of metals from ores with ultrasound, Mineral Processing and Extractive Metallurgy Review 16, (1997) 239-259.*
7. *K.M.Swamy, K.Sarveswara Rao, K.L.Narayana, J.S.Murty and H.S.Ray,Application of ultrasound in leaching, Mineral Processing and Extractive Metallurgy Review 14, (1995) 179-192.*
8. *K.M.Swamy, P.S.R.Reddy, K.L.Narayana, S.K.Biswal and J.S.Murty, Improvement in flotability of oxidised high ash Indian coals by ultrasound, Proceedings of International symposium on COAL-96, held at Dhanbad, India during Nov. 18-19, (1996) pp.199-210*
9. *K. M..Swamy, Industrial scale ultrasonic device for cleaning coal, Proceedings of International seminar on Mineral Processing Technology, held at Bhubaneswar during 28-30 Oct 2009, p81*
10. *K.M.Swamy, J.Muralidhar, K.L.Narayana and J.S.Murty, Effect of ultrasound on iron removal in reduced ilmenite, J.Acoustical Society of India 25, (1997) IV2.1-IV2.4*
11. *M.Misra, R.K.Mehta, Remediating heavy-metals, radionuclides and organic pollutants from soils, J.O.M., Journal of Minerals Metals and Materials Society, 47 (1995)45-53.*
12. *R.S.Steensma, Application of ultrasonics in the extraction of noble metals, in: A.E. Torma, I.H. Gundiler (eds), Process Metallurgy 5, Precious and Rare Metal Technologies, Elsevier, Oxford,1989,pp. 175-182.*
13. *Younggyu Son, Jihoon Cha, Myunghee Lim, Muthpandian Ashokkumar and Jeehyeong Khim, Comparison of Ultrasonic and Conventional Mechanical Soil-Washing Processes for Diesel-Contaminated Sand, Ind. Eng. Chem. Res., 2011, 50 (4), pp 2400–2407*
14. *A.F.collings, P.B.Gwan, CSIRO Telecmmunications & industrial physics, P.O.Box 218, Lindfield, NSW 2070, Australia, 2003.*
15. *Field Pilot Test of In-Situ Ultrasonic Enhancement Coupled With Soil Fracturing to Detoxify Contaminated Soil in Cooperation with McLaren/Hart Environmental Engineers at the Hillsborough, NJ Site, January 14, 1998.*
16. *Sami B Awad, Ultrasonic cleaning mechanism, Handbook for Critical Cleaning Cleaning Agents and Systems, Second Edition, Edited by Edward Kanegsberg CRC Press Chapter-13, pp 233-240.*
17. *Information supplied by Sonic Environmental Solutions Inc., Suite 1778 West 2nd Avenue, Vancouver, British Columbia, V6J 1H6, Canada.*
18. *Son Y, Nam S, Ashokkumar M and Khim J, Comparison of energy consumptions between ultrasonic, mechanical, and combined soil washing processes, Ultrason Sonochem, 2012 May;19(3):395-8. Epub 2011 Nov 23.*
19. *Thangavadivel, K, Megharaj, M, Smart, Lesniewski, PJ, Bates, D and Naidu, R, 'Ultrasonic enhanced desorption of DDT from contaminated soils', Water, Air and Soil Pollution, 217 (2011) 115-125.*

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WATER TREATMENT BY ADSORPTION THROUGH INDUSTRIAL SLUDGE

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ABSTRACT

Industrial effluents contain different heavy metals and as a step to pollution control it is necessary that proper treatment is carried out before its disposal. Out of many available methods, adsorption seems to be efficient and economically viable. The effluents might be containing heavy metals like Cu, Zn and Cd. In the present study attempts have been made to utilize an industrial sludge (which itself is a waste). Different parameters have been studied and adsorption isotherms have been fitted.

1. INTRODUCTION

Metallurgical, chemical and other plants discharge effluents containing different metals like copper, zinc and cadmium. It is necessary that these metals are removed before the water is discharged or reused. The process can be carried out by various methods of chemical precipitation, ion exchange, reverse osmosis and adsorption. Out of this adsorption has advantage over other methods because of low investment and simple design.

2. PROCEDURE

Waste sludge samples used in the experiments were procured from the industrial (steel industry) wastewater treatment plant, TISCO, Jamshedpur (India). The dried sludge samples were ground in a ball mill after drying and fractionated to W_1 (75 - 150 μm), W_2 (150- 425 μm), W_3 (425 - 850 μm) W_4 (850 - 1700 μm). Its bulk density and specific gravity were 0.85g/cm^3 and1.15 respectively.

Solutions of metal ions were prepared with nitrate salts of Zn $(NO_3)_2$ to eliminate the anionic effects. From the results of preliminary experiments and scanning of related literature it was decided that the following process parameters and experimental conditions should be maintained for all the kinetic studies.

Solution volume = 1000ml
Solution pH = 5.0
Particles size = W_1
Contact time = 3 hrs.

Amount of waste sludge= 2g / 1
Initial metal ion concentration = 20mg /1
Motor speed= 400 rpm

As adsorption proceeds , 5ml sample was withdrawn in the sample tubes after predetermined intervals of 0.5, 1, ,2, 5, 10, 35, 60,90,120,150 and 180 minutes and analyzed. All batches of kinetic studies were conducted at room temperature with a solution temperature in the range of 20-25^{0}C. In the initial stages of the adsorption studies, experiments were conducted alone with the metal solution without adding the adsorbent and metal-ions were analyzed with the AAS. Kinetic curves have been plotted with the amount of metal ions adsorbed in mg per gram of the adsorbent version time using equation (1).

$$q = (C_0 - C)\, V/m \qquad (1)$$

Where, q = Amount of metal-ion adsorbed or the sorption capacity, mg/g.
V= Volume of solution in liter,
m= Mass of adsorbent in gram
C_0= Initial metal-ion concentration in mg/1
C= Metal-ion concentration in mg/ 1
Percentage adsorption
Or
Percentage of metal-ion removal = $[(C_0-C) / C_0] X 100$

As the experiments were conducted little rise in the temperature was observed in every experiment, which might be due to the exothermic nature of adsorption reaction. (Weber, 1985)[1].

3. RESULTS AND DISCUSSIONS

3.1 Effect of contact time.

To study the adsorption kinetics, samples were withdrawn at different time intervals and analyzed

* About 25-30% of removal occurs within one minute for all the cases.
* Equilibrium time is achieved within 30 minutes.

It was also observed that uptake of metal-ion occurred in two stages i.e. an initial rapid uptake within 20 to 30 minutes followed by a subsequent slow uptake from 30 to 180 minutes. The required contact time increased with increased loading. The contact time required to reach equilibrium appeared to be proportional to the ratio of number of adsorption sites, to the number of metal species. (Netzer et al., 1984)[2]

3.2 Effect of initial metal-ion concentration

The kinetics of adsorption with waste sludge at different initial concentrations was studied. It was observed that the time to reach equilibrium increased with increase in initial metal-ion concentration in case of all the metal species. These observations were in agreement with Namasibayam et al., (1998) [3] It is concluded that by increasing metal-ion concentration the values of equilibrium time and sorption capacity were increased whereas the percentage of metal removal was reduced.

Table 1 Equilibrium time at different initial concentrations.

		Equilibrium time, minutes			
	Initial Conc.,mg/1	5	10	15	20
Metals	Cu (II)	20	30	60	60
	Zn (II)	20	60	90	90
	Cd (II)	20	30	30	30

3.3 Effect of particle size of adsorbent.

The kinetics of sorption of waste sludge for Cu (II), Zn (II) and Cd (II) at different particle sizes (W_1 W_2 W_3 and W_4) was studied. The experiments were conducted at pH 5.0 with an initial concentration of 20mg/1 and absorbent dose of 2g/1 . Time required for achieving equilibrium with different particle sizes are presented in the Table 2.

It is evident that the equilibrium time is increased with increasing size of adsorbent from W_1 to W_3 and became constant with further increase of size from W_3 to W_4 which was occurring in case of all the metals [Cu(II), Zn (II) and Cd (II)]. Erosa et al., (2001)[4] studied the influence of particle size on Cd (II) adsorption with chitosan and observed that equilibrium time was increased by increasing the size of the sorbent.

Table: 2 Equilibrium time for different particle sizes of waste sludge

		Equilibrium Times, minutes			
Particle Sizes		W_1	W_2	W_3	W_4
	Cu (II)	60	90	120	120
Metals	Zn (II)	90	90	120	120
	Cd (II)	30	60	120	120

The percentage removal decreased with increasing the size from W_1 to W_2 for all the metal species. It was observed that the metal ion removal efficiency was highest for the particle size W_1 and followed the following order Cu (II) > Cd (II) >Zn (II). It is concluded that equilibrium time, sorption capacity and the percentage of metal-ion removal decreased with increasing the particle size of waste sludge due to the availability of more surface area per gram of adsorbent. The process of adsorption with waste sludge might be a surface phenomenon as in case of Jha et al., (1988)[5].

3.4 Effect of sorbent dose.

The value of equilibrium time was found to be 60, 90 and 30 minutes for Cu (II), Zn (II) and Cd (II) respectively for the doses of sorbent in the range 0.25-2g/1. This value became 30, 60 and 30 minutes by increasing the dose up to 3 g/1. Further, these values decreased to 20, 30 and 20 minutes respectively by increasing the dose to 4 and 5 g/1. It revealed that the equilibrium time decreases with the increase in the concentration of waste sludge.

The metal removal efficiencies were found to be 32, 31.7 and 31.5% for Cu (II), Zn (II)and Cd (II) respectively. These values increased sharply to 85.3, 68.5 and 82.1 % respectively when the dose was increased to 2.0 g/1 . However , beyond the sorbent dose 2.0 g/1 up to 5.0 g/1 the increase in the percentage removal was marginal i.e. 8-10% for these metal ions. The order of adsorption was as follows. Cu (II) > Cd (II) > Zn (II).

Corapcioglu et al., (1987) [6] studied the removal of Cu(II), Ni (II), Pb (II) and Zn (II) by activated carbon and Esposito et al., (2001) [7] in biosorption of metal ions also reported such results.

3.5 Effect of rate of agitation.

The values of equilibrium time obtained were 90,60,90 minutes for Cu (II),90, 90, 60 minutes for Zn (II) 90,30,30 minutes for Cd (II)at agitation speeds 200,400 and 800 rpm respectively . From the results of equilibrium time it was observed that the time to attain equilibrium was reduced with the increase of agitation speed in case of all the metal species.

Increase in the speed of agitation decreased the boundary layer resistance to mass transfer in the bulk quickly or at less time. Thereby, it increased the driving force of metal-ions towards adsorption at less time. The process was influenced by the concentration gradient and the thickness of the diffusion layer, which was a function of agitation process. (Unninathan, M. et al., 2001)[8].

3.6 Effect of pH

It is well known that pH plays a vital role in the adsorption process. Metal-ions undergo adsorption at a different pH condition depending on the type and the form, of the adsorbent. Davis et al, (1978) [9] observed that adsorption of metal-ions on hydroxide surfaces are highly pH dependent. The pH was chosen as the master variable in the experimental studies of Benjamin et al, (1982)[10] and Balistreiri et al, (1982) [11]

In the present investigation the effect of pH was studied in the range 2.0 – 7.0 for different metal ions. It was observed that the time to approach equilibrium increased marginally with the increase of pH from 2.0 to 4.0 and thereafter remained constant up to pH 7.0 in case of all the metal ions [Cu(II), Zn(II) and Cd(II)]. Therefore, the effect of pH on removal kinetics seemed to be insignificant which is in agreement with the observations made by Chen et al., (2000) [12].

It was concluded that optimum pH should be within the adsorption edge and should have the lowest solution pH for maximum metal-ion adsorption and also should be near to pH of the solution prepared with metal salts. It is also well known that the pH of wastewater is generally in a slightly acidic range. Optimal pH value should also be such that the precipitation of metal-ions should not occur. Looking into all the characteristics of optimal pH, it was fixed at 5.0 for adsorption studies in the present work.

In an interesting observation, Cheung et al., (2000) [13] reported that the pH value at high concentration increased (initial pH to equilibrium pH) less than low concentration. This phenomenon might be explained by the availability of the cations to the sorption sites. When the low concentration solutions contained less metal-ion in the solution, more hydrogen ions would be adsorbed on the sorption sites. When the high concentration solution was used, enough cations can fill the sorption sites and less hydrogen ion would be adsorbed. Therefore, the pH at higher concentration increased less than in the low concentration solution.

3.7 Effect of Ionic Strength.

The effect of ionic strength on the sorption kinetics of waste sludge was studied by increasing the $NaNO_3$ morality from 0.001 to 0.1m, Equilibrium time was observed to be 90 minutes for adsorption in presence of ionic strength of 0.1 M of Na NO_3.

Influence of ionic strength of 0.1M showed that there was a reduction in metal removal to the tune of about 5.5, 21 and 20% for Cu(II), Zn(II) and Cd(II) respectively, where as these values were 0.8,2.6 and1.8 % at ionic strength of 0.001 M.

Chen et al., (1997) [14] in their adsorption with calcium alginate reported that Cu (II) removal decreased with increase in ionic strength. They observed that the functional groups become available at lower ionic strength at pH 5.0. However the increased ionic strength deactivate the functional groups of the adsorbent and hence% metal-ion removal is reduced. The decrease in adsorption at the higher ionic strength in the present work might be due to the above-mentioned reasons as these studies were conducted at a pH 5.0

3.8 Effect of anionic ligands.

Heavy metals are generally associated with anionic ligands in industrial effluents and wastewater. To minimize cationic effect sodium based anionic ligands were studied. These anionic ligands considered were EDTA, citrate, phosphate, acetate, fluoride and phosphate. It was observed that EDTA, is the strongest chelating agent among all the anionic ligands, which inhibited the uptake of metals even with a concentration of 0.1m M. These anionic ligands are multidentate ligands or ligand with more numbers of binding sites. The resulting metal complexes formed with these multidentate ligands (when react with metal-ions) are extremely stable because of higher stability constants for the corresponding metal-ions. These metal complexes cannot be adsorbed with the adsorbent (Blumeschein, C., 2000) [15].Wu et al (1999) reported that the selectivity sequence for Cu (II) ion adsorption with chitosan follows the following order EDTA > Tartarate > Citrate.

4. ADSORPTION ISOTHERM STUDIES

A proper contact between sorbate and sorbent is necessary for any adsorption process. Initially this concentration gradient at the sorbent surface is maximum . However, with time sorbate species starts migrating to the sorbent surface and concentration gradient start decreasing. After some time concentration gradient becomes negligible and there is no net transfer onto the sorbet. This establishes the dynamic equilibrium between sorbate and liquid phase and on the surface pf the adsorbent. Adsorption isotherm defines the equilibrium state.

As it is well known that adsorption of heavy metal-ions tend to be very sensitive to the particle size and pH; therefore, isothermal studies were carried out at different particle sizes i.e. W_1, W_2, W_3 and W_4 at pH 5.0 by varying initial concentration from 2 to 20 mg/ 1 using the procedure described earlier . The data obtained in the isotherm experiments have been fitted into two isotherm models i.e. Langmuir and Freundlich isotherm models.

4.1 Langmuir isotherm model

The linearised form of Langmuir isotherm equation is represented by the equation (2)

$$(C_e / q_e) = C_e / Q_0 + 1 / bQ_0 \qquad (2)$$

Where , 'Cc' and 'q_e' are the equilibrium sorbate concentration in the solution (mg/1) and in the solid phases (mg/g) where 'Q_0' represents the maximum adsorption capacity of the adsorbent (mg/g) and b represents energy ;of adsorption.

The values of 'Q_0' decrease from 11.49 to 10 mg/g for Cu (II), from 8.22 to 8.13 mg/g for Zn and from 9.35 to 8.2 mg/g for Cd (II respectively with the increase of particle size from w_1 to w_4. The values of 'b' were found to decrease from 1.1 to 0.34 1/gfor Cu(II) from 0.46 to 0.32 1/g for Zn(II) and from 1.39 to 0.68 1/g with the increase of particle size from W_1 to W_4 . The values of correlation coefficient were above 0.97 for Cu (II) except for W_4 i.e. 0.92. Similarly these values were above 0.94 for Zn (II) and above 0.96 for Cd(II) respectively. Therefore, Langmuir adsorption isotherm is found to be fitting for all the metal ions.

4.2 Freundlich isotherm model

The equilibrium adsorption data were also fitted to Freundlich equation. Adsorption of heavy metals with waste sludge follows Freundlich adsorption isotherm, which have been shown for Cu(II),Zn(II) and Cd(II) respectively using equation (3).

$$\ln q_e = (1/n) \ln C_e + \ln K_F \qquad (3)$$

Where, K_f and '1/n' are constants, which are considered to be the relative indicators of adsorption capacity and adsorption intensity.

The value of K_f decreases with the increase of particle size from W_1 to W_4. similar to these results, Jha et al. (1988) [5] reported that the K_f values decreases from 56 to 6.4 mg of Cd (II) per gram of chitosan with the increase of mean diameter of particle size from 37 to 328 µm. They concluded that these type of trend in the results show that there is good correlation between calculated ratio of specific surface areas and the experimentally determined adsorption capacity K_f for different particle sizes which is expected for non porous materials. Reduction in size greatly increases the surface area of such particles resulting in more removal of sorbate. The values of 1/n in Freundlich isotherm varies between 0.1 to 1.0 indicating favorable adsorption of heavy metals (Unninathan, M.et al, 2001) [8]and (Namasibayam et al, 1998) [3] The sorption equilibrium data follows Langmuir isotherm model. The maximum adsorption capacities are well compared with other adsorbents.

5. CONCLUSION

It may be concluded that industrial waste sludge (from steel plant) which itself is a waste product can be successfully utilized to adsorb the metal values like copper, zinc and cadmium from the effluents. Adsorption isotherm i.e. Langmuir and Freundlich were tried to study the sorption equilibrium and the former seems to be better fitting with the process. Further such studies can be taken up with waste sludge from effluent treatment plant of other industries. Pilot plant and scale up studies with actual metal contaminated waste water could be conducted in columns to know the practical utility in large scale applications.

REFERENCES

1. *Weber W J (Jr) adsorption theory concepts and models: cited in Adsorption Theory, F L Slejko (ed).Marcel Dekker Inc. N.Y (1985).*
2. *Netzer A and Hughes D E, Adsorption of Cu(II), Pb(II)and Co(II) by activated carbon. Water Res.18,927-933(1984).*
3. *Namasivayam C and Senthilkumar S, Removal of As(V) from aqueous solutions using industrial solid waste: Adsorption rates and equilibrium studies, Ind. Eng. Chem.Res.37,4816-4822(1988)*
4. *Erosa M S D, Mendina T L S, Mendoza R N, Rodriguez M A and Guibal E, Cadmium sorption on chitosan: Kinetics and equilibrium studies,Hydrmet,61,157-167 (2001)*
5. *Jha I N, Iyengar I and Rao A V S P, Removal of cadmium using chitosan, J Envir. Engg, ASCE,114 ,962-974 (1988)*
6. *Corapcioglu M O and Huang C P, Adsorption of heavy metals onto hydrous activated carbon. Water Res.,21 ,927-933(1987)*
7. *Esposito A, Pagnanelli F, Lodi A, Solosilo C and Veglio F, Biosorption of heavy metals by sphaerotilus natans: an equilibrium study at different pH and biomass concentrations. Hydromet.60,129-141(2001)*
8. *Unninathan M R and Anirudhan T S, The kinetics and thermodynamics of sorption of Cr(VI) onto the Fe(III) complex of a polyacrylamide-grafted saw dust, Ind Eng Chem Res,40,2693-3701(2001)*
9. *Davis J A and Leckie J O, surface ionization and complexation at the oxide/water interface:II surface properties of amorophous iron oxyhydroxide and adsorption of metal ions, J Coll Interface Sci, 67,90-107 (1978)*
10. *Benjamin M M and Leckie J O, multiple site adsorption of Cd,Cu,Zn and Pb on amorophous iron oxyhydroxide J Coll Interface Sci, 79,209-215 (1981)*
11. *Balistrieri L S and Murray J W, The adsorption of Cu(II), Pb(II) Zn(II) and Cd(II) on goethite from major ion seawater, Geochim.Cosmochim Acta 46,921-929 (1982)*
12. *Chen J P and Wang X removing Cu(II), Zn(II) and Pb(II) by granular activated carbon in pretreated fixed bed columns, Sep Purif Technol, 19, 157-167 (2000)*
13. *Cheung C W,Porter J F and Mckay G , Sorption kinetics analysis for the removal of cadmium ions from effluents using bone char, Water Res.,35(3),605-612(2000)*
14. *Chen J P, Tendeyong F and Yiacoumi S, Equilibrium and kinetics studies of copper ion uptake by calcium alignate, Environment Sci Technol 31,1433-1439 (1997)*
15. *Bluemenschein C D, Stae of art-activate water treatment technologies- zinc cadmium symposium ,US Filter, North American Technology Center, Idaho (2000).*

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UTILISATION OF WASTE MATERIALS IN DRI PROCESS

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INTRODUCTION

Generally we feed 1.6 to 1.7 tons of iron ore, 1 to 1.2 ton of coal and 0.025 to - 0.05 ton of dolomite or limestone to produce 1 ton of DRI/sponge iron. With the total input of 2.7 - 2.9 tons to the rotary kiln, the output is 1 ton of sponge iron and total waste is of order of 1.7 to 1.9 tons. Utilization of waste materials can be classified into three options.

- minimise the waste generation with in plant.
- use the generated waste within the plant to substitute the raw materials partly.
- Explore the use in other industries to substitute their raw materials.

The exhaustive study of all these the options will lead to wealth generation to the company.

Therefore it is important for any Process Engineer/Metallurgist to understand the breakup of these losses for exploring the possibilities of utilization all solid waste materials.

We have to understand first the basic chemical calculation, typical iron balance and carbon balance before making an attempt for a material balance of input and output.

Basic Chemical Calculation

Description	Iron ore in Kg	Sponge iron @90%met	Sponge iron in %	Iron ore in Kg	Sponge iron @90%met	Sponge iron in %
Fe total	60.00	60.00	88.20	67.00	67.00	92.00
Oxygen	25.70	01.70	02.50	28.70	02.00	02.80
Fe metal	-	54.00	79.40	-	60.00	82.40
Fe as Feo	-	07.70	11.30	-	07.00	12.40
Gangue	.06.30	06.30	09.20	03.80	03.8	05.20
LOI	08.00	-	-	0.50	-	-
Total	**100.00**	**68.00**	**100.00**	**100.00**	**72.80**	**100.00**

Typical Iron Balance

Description	Fe
Loss of Fe in DSC	0.6%
Loss of Fe in Waste gas dust	2.4%
Loss Of Fe in Oversize/accretion	0.7%
Fe in sponge iron	96.3%
Total loss of Fe	3.7%
Total loss of Fe2O3	5.29%

Typical Carbon balance

Description	Carbon in Kg/ton of Fe	percent
Kiln feed	480	100
Reduction	301	62.70
Non mag	80	16.70
DSC	09	1.90
ABC	49	10.20
Waste gas dust	13	2.70
Gasified	28	5.80

Sponge Iron

Generally the yield of sponge iron from the kiln feed shall be from 55% to65%. This wide variation is on account of quality of iron ore particularly Fe total, loss of ignition, gangue content and contaminants such as BHQ/porous/laterite etc.

Iron ore input on wet basis	1000 kg
Moisture loss (1%)	10 kg
Loss of iron ore (as per typical balance 6%)	60 kg
Loss of iron ore (iron ore fines -2mm 0.25%)	2.5 kg
Contaminants (BHQ etc 1%)	10 kg
Actual kiln input	917.5 kg
Sponge iron Yield (917.5*0. 0.728)	668 kg
Iron ore input (weigh feeder)	456 tons
Sponge iron produced (456 *66.8%)	304.61 tons

Char

Kiln input on wet basis	1000 Kg
Kiln input on dry basis(moisture 9%)	910 kg
Volatile Matter (26%)	237 kg
Ash (30.7%)	280 kg
Fixed carbon(43.2%)	393 kg
Carbon for reduction 393*62.7%	246 kg
Carbon burnt/gasified 393*20.6%	81 kg
Carbon in char	66 kg
Ash in char: (280-50-12)	218 kg
Volatile matter in char (237*3%)	7 kg
Non magnetic (66+218+7)	291 kg
Coal input (weigh feeder)	360.00 tons
Char produced (360*0.291)	104.76 tons
Dolomite input	7.20 tons
Quantity of calcined dolo(7.2*0.6)	4.32 tons
Contaminants from iron ore (456*0.01)	4.56 tons
Total char produced	113.64 tons
Total cooler discharge 304.61+113.64	418.27 tons
Non mag. percentage (113.64/418.27)	27.16%

Based on actual weighment of char on monthly basis, we found the generation of char is varying from 90 tons to 100 tons per day and bag filter dust as 15 to 20 tons per day.

Loss of material in ESP and DSC

Loss of iron ore in DSC/ESP at 456*5.3%:	24.17 tons
Loss of iron ore fines at 456*0.25%:	1.14 tons
Loss of carbon and ash in DSC/ESP(360*(1.8%+5%)):	24.48 tons
Total loss:	**49.79 tons**

This loss of materials in DSC/GCT/ESP can also be calculated based on daily/monthly weighment of materials. Based on this weighment, the average daily generation is 5 tons for DSC and 15 tons for GCT and 30tons for ESP.

Accretion

The iron ore fines and coal ash forms low melting compound during the operation of kiln and adhere to the refractory wall,

Loss of Iron ore in accretion 456*0.7%	3.19tons
Loss of coal ash in accretion 360*1.2%	4.32 tons
Total accretion	**7.51 tons**

We have weighed the accretion for many campaigns of the order of 150 to 200 tons during the campaign of 50 days average.

This has been calculated as 3 to 4 tons accretion formation for each operating day.

O_2 losses

Sponge iron produced	304.61 tons
Fe total in sponge iron 304.61*92%	280.24 tons
O_2 removed (280.24*0.429*0.95)	114.21 tons

The presence of oxygen in Fe_2O_3 is 0.429 ratio, based on this chemical calculation the loss of oxygen per day is determined as total sponge iron produced *Fe total in sponge iron *0.429 is oxygen loss*degree of reduction at 95 percent.

Loss on Ignition

Iron ore contains some percentage in the form of hydroxides and organic matter, known as loss on ignition. These constituents are liberated at temperature of above 900°C the percentage of loss on ignition various from 0.5% in high grade iron ores to level of 12% in laterite and porous type of iron ores.

Iron ore input	456 tons
Loss of ignition 456*0.5%	2.28 tons

Volatile matter from coal

Coal contains volatile matter mainly in the form of hydro carbons which are liberated above 400°C. The volatile matter (97%) is burnt either in the kiln or in the after burner chamber. The loss on volatile mater calculated as total coal fed in to the kiln per day *the percentage of VM in the coal.

Total coal input	360 tons
Volatile matter 360*23.7	85.32tons
Volatile matter burnt at 97%	82.80 tons

Moisture from coal

Coal contains 2 to 3% of inherent moisture and5 to 6% of surface moisture. The total moisture liberated in the from steam in waste gases. The total moisture loss from coal is calculated as coal fed in to the kiln *% total moisture.

Total coal input	360 tons
Moisture released 360*9%	32.40 tons

Moisture Iron ore

Generally iron ore contains very low moisture of less than 1% ; however during the rainy season and/or with dust suppression the moisture level is in the range of 2 to 4%. The moisture is liberated in form of steam in waste gases.

Iron input to the kiln	456 tons
Moisture at 1%	4.56 tons

Burning of carbon

As explained earlier carbon input in to the kiln is utilized primarily for reduction purpose. Some carbon is burnt for heating purpose in the preheating zone as well as carbon dust burned in the ABC.

Carbon for reduction (360*39.3%*63%)	88.70 tons
Carbon burnt in the kiln and ABC (360*39.3%*16%)	22.64 tons

Calcinations of Dolomite

Dolomite contains 25 to 35% calcium carbonate 10 to 15% magnesium carbonate. The loss on account of calcinations of the dolomite is 40%by weight.

Total dolomite input per day	7.2 tons
Loss on calcinations (7.2*0.40)	2.88 tons

Input/output

Based on this calculation the material balance for the input raw materials and output product/waste products was calculated as given below.

Input raw materials in tons

Iron Ore:	456.00
Coal:	360.00
Dolomite:	7.2
Total:	823.20

Product /Solid Waste/Waste Gases in tons

Sponge Iron	304.61	36.87%
Char	93.64	11.34%
Bag filter Dust	20.00	2.42%
Wet Scrapper Dust	5.00	0.60%
ESP/GCT Dust	44.79	5.42%
Accretion	7.51	0.91%
O_2 Loss	114.21	13.82%
LOI	2.28	0.30%
VM from Coal	82.80	10.02%
Moisture from Coal	32.40	3.92%
Moisture from Ore	4.56	0.55%

Burning of Carbon	111.34	13.48%
Dolomite cal.	2.88	0.35%
Total output	**826.02**	**100%**
Input-Output	+2.82	+0.34%
Solid Wastes	170.94	20.69%
Waste Gases	350.47	42,42%

Char:

The generation of char in a 350tpd plant is of the order of 90-100tons per day which is 55 percent all solid wastes generated. We have done the study of proximate analysis grain size wise and the calorific value for 0-4mm fraction and 4-10mm fraction. The analysis is as given below.

Size fraction	Percent	VM	Ash	Fixed carbon	GCV
+8mm	10.38	0.97	88.92	10.11	2200
+6mm	6.60	1.97	69.81	28.22	
+4mm	9.43	4.07	63.14	32.79	
+2mm	11.32	3.54	60.98	35.48	3000
+1mm	20.45	3.58	51.99	44.43	
-1mm_	41.52	3.00	57.02	39.98	

Based on this analysis char fraction of 0-4mm and 4-10mm can be utilized in AFBC boilers to substitute coal to an extent of 25 – 30 percent. The limitation is on account of contaminants in the form of mgnetics and coal ash/stone pieces. These can be effectively separated using high intensity magnetic separators of 2500 gauss and by using air jigging.

The stone contaminants is generally in the fraction of plus 8mm which can be removed by simple screening and 4-8mm can be used in the process to substitute the feed coal by 5percent.

Char is also used as fuel in brick kilns and as domestic fuel in the form char briquettes.

Bag filter dust:

The bag filter dust collected in the cooler discharge bag filter is around 15 to 20 tons per day and in the size range of 50 to 100 microns. The proximate analysis indicate fixed carbon in the range of 30 to 35 percent.

Size analysis in microns					Proximate analysis in percent		
+230	+150	+100	+80	-80	VM	Ash	FC
2.00	1.69	2.87	3.20	90.24	1.51	61.50	36.99

We have studied the possibility of using this material to substitute activated carbon. The MB value of this dust is found to be in the order of 100 – 140. The contaminant is micro fine iron dust which is to be controlled. This dust is also utilized in agarbatti industries to substitute carbon dust. As the calorific value is plus 3000kcal/kg, sponge iron plants with waste heat recovery boilers are using this dust in the after combustion chamber for additional steam generation as well.

Kiln back flow material:

Even with the best operating conditions in the sponge iron plant, some quantity of coal spills out from the inlet of the rotary kiln. The quantity is of the order of 5tons per day including the dust from Dust settling chamber. The proximate analysis of this material is as given below.

Size analysis		Proximate analysis		
Size fraction	percent	VM	Ash	Fixed Carbon
+4mm	83.06	21.11	52.02	26.87
-4mm	16.94	13.63	50.32	36.05

The total quantity of plus 4mm fraction of the back flow can be used to substitute the feed coal in the process. The minus 4mm material can be used in brick kilns as a fuel.

Gas Conditioning Tower sludge:

The quantity of GCT sludge is of 15tons per day. At present this material is used only for filling up low lying areas. UNIDO has done a study of the use of this materials for the manufacture of floor tiles at SPONGE IRON INDIA LTD. This aspect is to be further explored for use of this material in the manufacture of fly ash bricks and tiles. The chemical analysis of this sludge is as given below.

Proximate analysis of GCT sludge in percent			
Volatile matter	Ash	Fixed carbon	Fe Total in Ash
3.8	92.69	2.50	15.28

ESP dust:

The dust collected in ESP hoppers of size below 50 microns is of the order of 30 tons per day.The use of this dust for making of fly ash bricks is an established practice now. The limitation is that the percentage of carbon has to be within 5percent for fly ash brick manufacture. If the carbon can be controlled within 1.5% this fly ash can also be used in the manufacture AC sheets to substitute cement.

Proximate Analysis of ESP dust in percent			
Volatile matter	ash	Fixed carbon	Fe Total in Ash
2.89	93.81	3.30	15.73

Waste Gases

With the release of moisture from iron ore and coal, calcination of dolomite, removal of oxygen from the iron ore and combustion of volatile matter from coal, the waste gases leaving the kiln in 350tpd kiln is of the order of 85000Nm3/hr at 900-950 deg.C. With the sensible heat of the waste gases and chemical heat contributed by burning carbon and carbon monoxide in the after burner chamber, we can generate 35tons of steam to support 8MW power generation. With the new development on preheating technology, the waste gases are utilized for preheating the iron ore resulting in reduction in coal consumption by 10percent.

CONCLUSION:

In the process of manufacture of sponge iron, 2.71tons of input raw material results in solid wastes of 0.56 tons and 1.15tons of waste gases for one ton of sponge iron. Detailed granulometric and chemical characteristics were determined for proper utilisation of all the solid waste materials generated in the sponge iron industry.
Tested and proven practices have been incorporated for utilization of 80 percent of solid wastes and utilization of 100 percent of waste gases. With these practices, wealth can be certainly generated from waste materials in sponge iron industry.

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MICROBIAL REDUCTIVE DISSOLUTION: A NEW APPROACH FOR EXTRACTION OF METAL VALUES FROM LATERITES

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ABSTRACT

Lateritic minerals represent the most abundant reserve of nickel in the earth crust. These are oxidic minerals in which nickel is closely associated with ferric iron minerals, such as goethite [FeO(OH)]. Microbial processing of laterites have been investigated for extraction of metal values, however an economically viable process has not been developed so far. The present study deals with the use of bacterium Acidithiobacillus ferrooxidans (isolated from mine water) for microbial extraction of nickel from lateritic chromite overburdens (COB), Sukinda. The bacterium facilitated extraction of nickel from lateritic COB through the microbial reductive dissolution of host ferric iron (goethite) minerals under anoxic environment. In anoxic environment, A. ferrooxidans reduced the ferric iron in goethite [Fe(O)OH] mineral of COB by using elemental sulphur as electron donor. Nickel embedded in the complex goethite [Fe(O)OH] matrix of COB was successfully recovered by cumulative action of sulphuric acid, generated by oxidation of elemental sulphur and reduction of ferric iron in goethite matrix by A. ferrooxidans. About 41% of nickel present in COB was extracted in a 3L scale bioreactor maintained in anoxic environment (pH-1.8±0.05, temperature- 28 ±2°C).

Keywords: *Acidithiobacillus ferrooxidans, Nickel, Laterites, Reductive dissolution,*

1. INTRODUCTION

Waste generated from mining and mineral operations was considered as the mineral containing materials which are no longer required for extraction of metals in industrial scale. Being a mineral rich country, India has generated around 1840 million tonnes of mining waste in year 2005-06 alone (Sahu and Dash, 2011). Sukinda valley in the state of Odisha is one of the major chromite reservoirs of the world and is the only known deposit of nickel in India (Rama Murty et al. 2010). Chromite mining at Sukinda valley annually generates around 6 to 7 million tonnes of lateritic chromite overburdens (COB) containing nickel (0.5 to 1.0%) (Swain et al. 2007). Nickel ores are generally classified into two types *i.e.* (i) sulphide and (ii) lateritic (oxidic) type. The sulphidic ores are industrially exploited for extraction of nickel throughout the globe, whereas the lateritic ore is hardly utilised because of its mineralogical complexities. Furthermore, unexploited lateritic deposits in the earth crust have occupied the most abundant reserves (>70%) of nickel existing in the globe (Simate et al. 2010). Nickel present in laterites lack discrete mineral phase rather it is closely embedded with iron mineral matrixes [(goethite, FeO(OH)] (Swamy et al. 2003). Hence due to such mineralogical complexities the conventional metallurgical technologies have not been so far industrially accepted for extraction of nickel from laterites (Valix et al. 2001). However, due to rapid increase in nickel consumption coupled with gradual depletion of sulphidic mineral reserves of nickel, exploitation of the laterite deposits for the extraction of nickel has become inevitable. Hydrometallurgical operations involve in extraction of metals from lateritic minerals are generally conducted through solubilisation of metals by mineral acids (sulphuric, hydrochloric acids). However substantial amount of metal recovery from laterites have been achieved only through thermal pre-treatment of laterites, using higher concentrations of acids and leaching at elevated temperature (Li et al. 2009; Luo et al. 2011; McDonald and Whittington, 2008; Girgin et al. 2011). In this context microbial processing at ambient conditions can reduce acid and

energy consumption in the metal extraction from laterites.

Microorganisms such as bacteria and fungi can convert metal compounds into their water-soluble forms through the microbes-minerals interaction at ambient conditions. Furthermore, by applying microorganisms such as species of *Aspergillus*, *Penicillium*, *Acidithiobacillus*, *Leptospirillium* etc. it is possible to recover metal values from low grade minerals as well as the industrial wastes having trace amount of metal values (Das et al. 2011). Microbial application for processing of laterites for nickel extraction has been extensively studied by using several acid producing heterotrophic fungal species of *Aspergillus* and *Penicillium*. Physiological activities of the microbes produce organic metabolites such as citric and oxalic acids. These organic acids are metal chelating in nature and hence are involve in mineral solubilisation (Bosecker, 1997). However, certain drawbacks are associated with the use of such heterotrophic microorganisms in large scale operation of mineral processing like the cost of microbial nutritional substrates (glucose or carbohydrate source) required for organic acid production is high. Further the excess production of microbial biomass coupled with relatively poor yield of metal values is also a matter of concern.

The classical oxidative bioleaching mechanism involves the application of chemolithotropic bacteria belonging to the genus *Acidothiobacillus* for bioleaching of sulphide ores. The oxidative bioleaching mechanism involves the production of Fe^{+3} ion from the bio-oxidation of Fe^{+2} by *Acidithiobacillus* bacterial strain (Chen et al. 2011). In brief, the two proposed mechanisms namely thiosulphate mechanism and polysulphide mechanism are applicable for the oxidation of acid insoluble metal sulphides [pyrite (FeS_2) and molybdenite (MoS_2)], and for acid soluble metal sulphides [sphalerite (ZnS), chalcopyrite ($CuFeS_2$)], respectively (Schippers and Sand, 1999; Rohwerder et al. 2003). Such bio-oxidation process is hardly applied for the bioleaching of lateritic ores. Recent findings suggest that bacterial strains of *Acidithiobacillus* have been found to be more effective in dissolution of nickel from laterites (Hallberg et al. 2011). Under anoxic condition these acidophilic bacteria mediate reduction of ferric iron with simultaneous production of sulphuric acid by oxidation of elemental sulphur, organic compound and reduced inorganic sulphur compounds (Johnson and Hallberg, 2009; Rawlings, 2005).

The present work focuses on the efficient utilisation of lateritic COB for extraction of nickel *via* anoxic reductive microbial processing by *A. ferrooxidans*. Anoxic reductive method is a new and novel approach for processing of lateritic minerals (ferric rich) by using *A. ferrooxidans*. This bacterium reduces ferric iron to ferrous iron in anoxic condition with a suitable electron donor (elemental sulphur) and produces sulphuric acid. In the present study, the experiments were performed in 3L bioreactor maintained in anoxic condition for the reduction of ferric iron in goethite [FeO(OH)] mineral of COB by *A. ferrooxidans* using elemental sulphur as electron donor to extract nickel.

2. MATERIALS AND METHODS

2.1. Lateritic nickel ore Samples

Lateritic chromate overburden (COB) samples were collected from Sukinda mines of the state Odisha, India. The COB ore samples were crushed by using agate mortar and pestle and the crushed samples were sieved through a mesh (BSS-25) to obtain particle size of -599 µm. The lateritic COB has the following metal composition: nickel, 0.99%; iron, 48.88%; cobalt, 0.03%; chromium, 2.59%; manganese, 0.21%.

2.2. Microorganism

Bacterial strain of *A. ferrooxidans* was isolated from the Turamdih mine water sample. Prior to the experiment, the bacterial strain was activated by repeated sub-culturing in $9K^+$ medium containing g/L: $(NH_4)_2SO_4$ - 3, $MgSO_4.7H_2O$ - 0.5,

KH_2PO_4 - 0.5, $FeSO_4.7H_2O$ - 44.2 (Silverman and Lundgren, 1959). After sub-culturing, a steady state of iron oxidation rate (600 $kg/m^3/hr$) was achieved. This activated form of bacterial culture was taken for conducting the further experiments.

2.3. Bioreactor

Experiments were conducted in a 3L single-stage bioreactor (Fig. 1), made up of borosilicate glass and equipped with a stirrer and air sparger. The bioreactor had a height/diameter ratio ≈ 2:1 and a working volume of 2L. The bioreactor was designed with a flat bottom and air tight lid. Air flow was controlled by inlets and outlets for maintaining desirable environment inside the reactor. For aerobic microbial processing, air is normally supplied whereas, for maintenance of anoxic condition the air inside the reactor was pumped out by vacuum pump followed by sparging of inert nitrogen gas till the complete removal of dissolved oxygen in the culture medium. The flow of air was controlled by an airflow meter and the agitation speed by a magnetic stirrer.

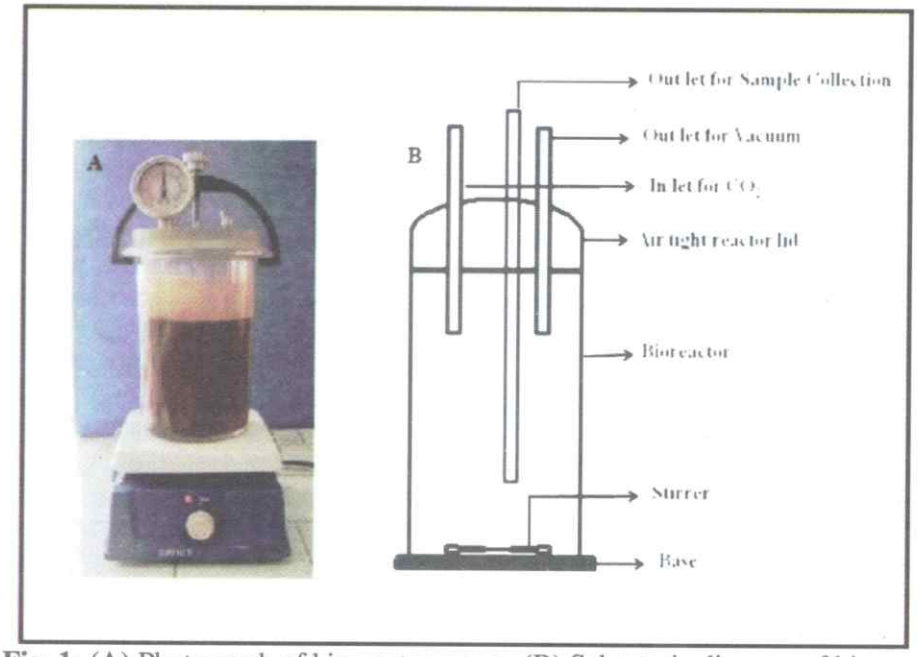

Fig. 1: (A) Photograph of bioreactor set up, (B) Schematic diagram of bioreactor

2.4. Microbial processing

The microbial processing of the lateritic nickel ore in the bioreactor was conducted under anoxic condition. To the bio-reactor 100g of COB and two litres of 9K medium were taken. Activated bacterial inoculum (*A. ferrooxidans*) ($\approx 10^6$ spores/mL) along with elemental sulphur was added into the bioreactors at 10% (v/v) and 2% (w/v) concentration, respectively. The anoxic microbial reduction experiment was performed with an initial pH of 1.8±0.05, temperature of 28 ±2°C, agitation speed of 150 rpm and an incubation period of 24 days. Likewise, a control experiment was performed keeping all the parameters intact as that of the previous experiment except the inoculation of microorganism (*A. ferrooxidans*). Samples were drawn from bioreactor through a sample collecting valve for analytical studies at 3 days interval.

At the end of the anoxic microbial reduction experiment, oxygen free nitrogen supply and stirring of the bioreactor was halted. The remaining lateritic COB was physically separated from the sedimented residual sulphur, and was further washed. The ore was washed with dilute H_2SO_4 (pH-2) to remove the metals adsorbed to the surface of the COB leach residue. Further, the metal ion concentration in the leached liquor was

determined by atomic absorption spectrophotometer (AAS) (Perkin Elmer-AA200, USA).

The bacterial cell count was carried out at 3 days interval to record the number of active bacterial cells present in bioreactors. Live bacterial cells in samples drawn from bioreactors were counted with a Petroff Hauser counting chamber (Hausser Scientific, USA) by using a phase contrast microscope (Nikon-Eclipse 80i, Japan). Aeration to the culture in bioreactor was supplied until the bacterial cell count attained a desired strength (10^8cells/mL). After the desired strength of bacterial cell count was achieved aeration was stopped for microbial processing.

2.5. Analytical methods

The samples of COB were air dried and the metal contents were determined after acid digestion. Samples drawn from the bioreactors at 3 days interval were immediately subjected to filtration by using 0.22µm membrane filter followed by estimation of nickel, ferrous, total iron and sulphate ion. Nickel concentration was determined by using AAS. Concentration of ferrous iron was analyzed by titration method using 0.1N potassium dichromate as titrant and barium diphenylamine-4-sulfonate (BDAS) as redox indicator. The concentration of ferric iron was calculated by subtracting concentration of ferrous ion from total iron (Vogel, 1961).

Mineralogical analysis of original and leach residues were carried out to identify major and minor minerals by means of X-ray diffraction study (Phillips Diffractometer - PW3710) with a radiation operating at 40 kV and 30 mA.

The SO_4^{-2} ions generated in response to oxidation of elemental sulphur during the experiments were estimated by Ion-exchange chromatograph (Metrohm, equipped with Column Metrosep A Supp 5 - 250/4.0). The mobile phase used for elution of anions was composed of 3.2 mM Na_2CO_3 and 1mM $NaHCO_3$ in Millipore water. The flow rate of the mobile phase was maintained at 0.700 mL/min and column pressure of 12.94 MPa.

The pH of the bioleach liquor was constantly monitored by a pH meter (Systronics, India). Before microbial processing the pH was adjusted to 1.8 with dilute H_2SO_4 (0.1 M) as the considered bacterial strain is pH dependent *i.e.* below 2.0.

3. RESULTS AND DISCUSSION

3.1. Mineralogical analysis

The X-ray diffraction spectrum (Fig. 2) of the COB indicates the presence of goethite as major iron mineral phase in COB. It was deciphered that the nickel occurs in an absorbed state within the goethite matrix of COB (Sukla and Das, 1987). However after completion of microbial processing (24 days) the X-ray diffraction study of leached residue showed the presence of magnetite ($FeO.Fe_2O_3$) peaks. Mineralogical analysis of the leached residue obtained after anoxic microbial processing indicated that the ferric iron of goethite was reduced to ferrous form in presence of sulphur (electron donor).

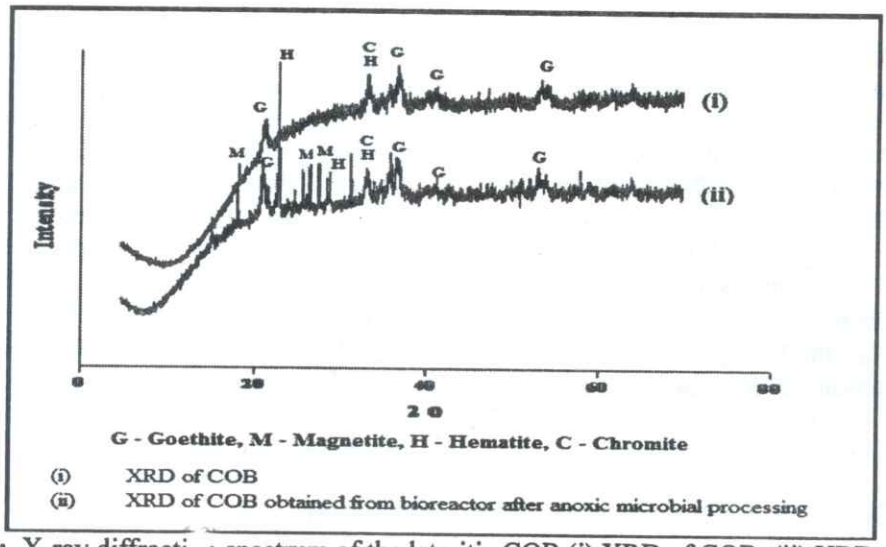

Fig. 2: X-ray diffraction spectrum of the lateritic COB (i) XRD of COB, (ii) XRD of COB obtained from bioreactor after anoxic microbial processing.

3.2. Nickel Extraction

Fig. 3 depicts the extraction of nickel, dissolution of iron and bacterial cell count in a regular interval (3 days) during microbial processing of COB. Nickel extraction increased up to 18 days and further it remained almost static till the end of the experiment. Similar trend was observed in case of iron dissolution. The microbial processing experiments showed that up to 41% nickel extraction was achieved in 18 days from COB (1% nickel grade) at 5% pulp density. Mohapatra et al. (2007) demonstrated 40% recovery of nickel from COB at 2% pulp density by conducting bioleaching with *A. ferrooxidans* but the drawback lies in the roasting (400°C for 5hr) *i.e.* pre-treatment of COB. Several studies have been conducted to facilitate substantial recovery of nickel *via* thermal pre-treatment of laterites (Li et al. 2009; Mohapatra et al. 2008). Our study reports higher amount of nickel recovery from COB compared to other studies conducted with thermal pre-treated COB. Similarly, iron dissolution from the nickel laterite was concomitant with the nickel extraction. *A. ferrooxidans* reduced the ferric iron of goethite [FeO(OH)] phase of the COB when incubated under anoxic conditions in presence of sulphur.

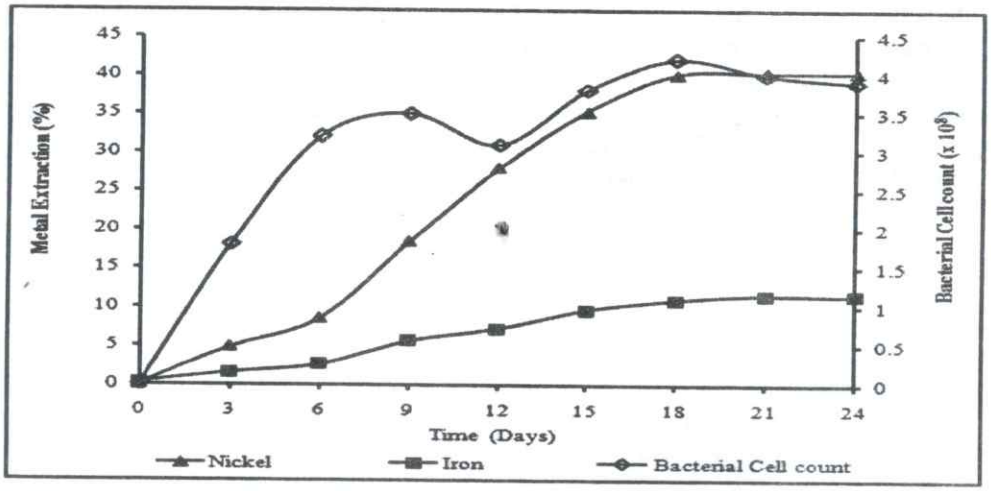

Fig.3: The Plot showing nickel and iron extraction (%) and bacterial cell count as a function of time from lateritic COB by using *Acidithiobacillus ferrooxidans* in bioreactor during microbial processing

Sulphur used in the medium for *A. ferrooxidans* acts as the source of electron for chemolithotropic mode of nutrition (Kucera et al. 2012). Concentration of Fe^{+2} ions generated due to reduction of Fe^{+3} in the goethite during the microbial processing is shown in Fig. 4. In sulphate media Fe^{+2} is quite stable upto pH≈5. Since the present study was performed at pH≈1.8 so all the Fe^{+2} generated would be in the solution as ions and there is no possibility of its precipitation (Johnson et al. 2012). Fe^{+3} in the goethite phase was reduced to Fe^{+2} by the elemental sulphur (electron donor) during the anoxic reduction of COB and the sulphur was oxidised to hydrogen sulphate (HSO^-_4) (which subsequently was converted to H_2SO_4) that generated acidity in the medium and was responsible for dissolution of nickel and iron from the COB. It has been observed that generation of H_2SO_4 *via* HSO^-_4 resulted in lowering the pH of the medium in bioreactor. This can be explained by Eq. 1 as reported by Brock and Gustafson (1976).

$$S^0 + 6Fe^{+3} + 4H_2O \longrightarrow HSO^-_4 + 6Fe^{+2} + 7H^+ \quad \text{(Eq. 1)}$$

Under aerobic condition oxygen behaves as a terminal electron acceptor during chemolithotrophic mode of respiration because ferrous iron in acidic environment is spontaneously oxidised to ferric iron and generates free electron. Further, Fe^{+2}/Fe^{+3} redox couple has a very positive standard electrode potential (+770mV at pH 2) which is close to the standard electrode potential of O_2/H_2O redox couple (O_2/H_2O: +820mV at pH 7) as a result, only oxygen bears the potentiality to act as a natural electron acceptor in the presence of protons to be reduced to water (Rawlings, 2005).

Higher yield of nickel (41%) during anoxic microbial processing was due to the cumulative effect of *A. ferrooxidans*–COB interaction and the acidic (H_2SO_4 generated during the microbial processing) property of the media. In contrast, the control experiment performed in anoxic conditions showed 3-3.5% nickel and 0.20-0.25% iron dissolution after 24 days.

3.3. Ion-exchange chromatography

The ion chromatography analysis carried out for the samples drawn from bioreactors revealed that, 0.51 M/L sulphate was produced from the oxidation of elemental sulphur during the microbial processing (Fig. 4). The figure shows that the sulphate production improved significantly by the oxidation of elemental sulphur after a brief lagging period of 4 days. Further from 4th day onwards, sulphate production was enhanced concomitantly with nickel extraction in anoxic condition. The chromatography study indicated that the acidity generated due to oxidation of elemental sulphur coupled with the reduction of the ferric iron in COB favoured the nickel extraction. Due to reduction of ferric mineral in COB, it was more susceptible towards lixiviant, as a result of which the nickel associated with goethite phase of COB was successfully leached out by microbial processing.

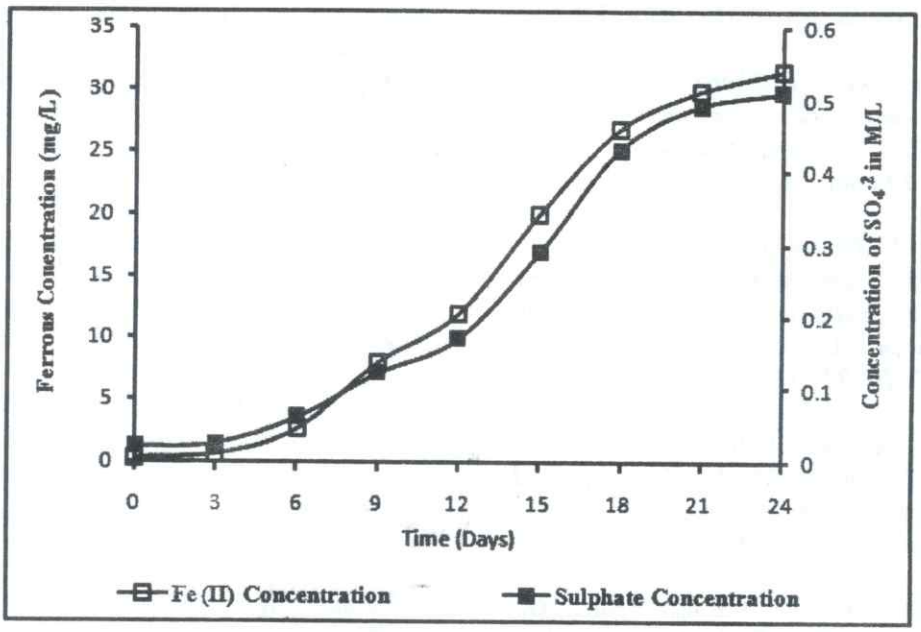

Fig. 4: Estimation of sulphate ion and ferrous iron concentration during the microbial processing of lateritic COB.

4. CONCLUSION

Extraction of nickel from the COB of Sukinda by anoxic microbial processing is a benevolent approach in the field of mining waste utilization. Further the process has been carried out without any thermal pre-treatment or activation of COB prior to microbial processing; those are known to be environmentally unfriendly and energy intensive. This avenue probably provides the maximum extraction of nickel (41%) from COB (1% nickel grade) without any pre-treatment. The anoxic microbial processing is an attractive process for utilization COB and has a scope and prospect of industrial application.

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REFERENCES

Bosecker, K., 1997. Bioleaching: metal solubilization by microorganisms. FEMS Microbiol. Rev. 20, 591–604.

Brock T.D., Gustafson, J., 1976. Ferric iron reduction by sulphur and iron-oxidizing bacteria. Appl. Environ. Microbiol. 32, 567–571.

Chen, P., Yan, L., Leng, F., Nan, W., Yue, X., Zheng, Y., Feng, N., Li. H., 2011. Bioleaching of realgar by Acidithiobacillus ferrooxidans using ferrous iron and elemental sulfur as the sole and mixed energy sources. Bioresour. Technol. 102, 3260–3267.

Das, A. P., Sukla, L. B.,. Pradhan, N., Nayak, S., 2011. Manganese biomining: A review, Bioresour. Technol. 102, 7381-7387.

Girgin, I., Obut, A., Ucyildiz, A., 2011. Dissolution behaviour of a Turkish lateritic nickel ore. Miner.Eng. 24, 603–609.

Hallberg, K. B., Grail, B. M., Plessis, C. A., Johnson, D. B., 2011. Reductive dissolution of ferric iron minerals: A new approach for bio-processing nickel laterites. Miner.Eng. 24, 620–624.

Johnson, D. B., Kanao, T., Hadrich, S., 2012. Redox transformations of iron in

extremely low pH: fundamental and applied aspects. Front. Microbiol. 3, 1-13.

Johnson, D.B., Hallberg, K.B., 2009. Carbon, iron and sulfur metabolism in acidophilic micro-organisms. Adv. Microb. Physiol. 54, 202–256.

Kucera, J., Zeman, J., Mandl, M., Cerna, H., 2012. Stoichiometry of bacterial anaerobic oxidation of elemental sulfur by ferric iron. Antonie Leeuwenhoek DOI 10.1007/s10482-012-9699-x

Li, J., Li, X., Hu, Q., Wang, Z., Zhou , Y., Zheng, J., Liu, W., Li, L., 2009. Effect of pre roasting on leaching of laterite. Hydrometallurgy 99, 84–88.

Luo, W., Feng, Q., Ou, L., Zhang, G., Chen, Y., 2010. Kinetics of saprolitic laterite leaching by sulphuric acid at atmospheric pressure. Miner. Eng. 23, 458–462.

McDonald, R.G., Whittington, B.I., 2008. Atmospheric acid leaching of nickel laterites review.Part II. Chloride and bio-technologies. Hydrometallurgy 91, 56–69.

Mohapatra, S., Sengupta, C., Nayak, B. D., Sukla, L. B., Mishra, B. K., 2008. Effect of thermal pretreatment on recovery of nickel and cobalt from Sukinda lateritic nickel ore using microorganisms. Korean J. Chem. Eng. 25(5), 1070-1075.

Mohapatra, S., Bohidar, S., Pradhan, N., Kar, R.N., Sukla, L.B., 2007. Microbial extraction of nickel from Sukinda chromite overburden by Acidithiobacillus ferrooxidans and Aspergillus strains. Hydrometallurgy 85, 1–8.

Murthy, Y. R., Rao, B. C., Kapure, G., Tathavadkar, V., 2010. New prospective for the utilisation of Indian lateritic chromite overburden. Proc. XI Int. Sem. Miner. Process. Technol. India, 158–165.

Rawlings, D. E., 2005. Characteristics and adaptability of iron- and sulfur-oxidizing microorganisms used for the recovery of metals from minerals and their concentrates. Microb. Cell Fact. 4, 13.

Rohwerder, T., Gehrke, T., Kinzler, K., Sand, W, 2003. Bioleaching review part A: Progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation. Appl. Microbiol. Biotechnol. 63, 239–248.

Sahu, H. B., Dash, S., 2011. Land degradation due to mining in India and its mitigation measures. Proc. 2nd Int. Confer. Environ. Sci. Technol. Singapore, 6, 132-136.

Schippers, A., Sand, W., 1999. Bacterial leaching of metal sulphides proceeds by two indirect mechanism via thiosulphate or via polysulphides and sulphur. Appl. Environ. Microbiol. 65, 319–321.

Silverman, M.P., Lundgren, D.G., 1959. Studies on the chemoautotrophic Iron bacterium Ferrobacillus ferrooxidans. An improved medium and a harvesting medium for securing high cell yields. J. Bacteriol. 77, 642–647.

Simate, G. S., Ndlovu, S., Walubita, L. F., 2010. The fungal and chemolithotrophic leaching of nickel laterites — Challenges and opportunities. Hydrometallurgy 103, 150–157.

Sukla, L.B., Das, R.P., 1987. Kinetics of nickel dissolution from roasted laterites. Trans. Indian Inst. Met. 40, 351–353.

Swain, P. K., Chaudhury, G. R., Sukla, L. B., 2007. Dissolution kinetics of chromate overburden by using mineral acids. Korean J. Chem. Eng. 24 (6), 932-935.

Swamy, Y.V., Kar, B. B., Mohanty, J.K., 2003. Physico-chemical characterization and sulphatization roasting of low-grade nickeliferous laterites. Hydrometallurgy 69, 89–98.

Valix, M., Usai, F., Malik, R., 2001. Fungal bio-leaching of low grade laterite ores. Miner. Eng.14 (2), 197-203.

Vogel, A.I., 1961: A Text Book of Inorganic Analysis. Longman, New York.

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WASTE TO WEALTH PROBABILITY : THE MINES & MINERALS SCENARIO

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ABSTRACT

Globally estimated waste production for 2010 was around 20 Billion Tonnes comprising the sum total of organic, inorganic, hazardous and nonhazardous, industrial, mining-metallurgical, municipal and other miscellaneous rejections. Asia alone was responsible for 4.4 Billion Tonnes and out of that, China shared 1.2 Billion Tonnes while India owned up the gross tonnage of a Billion Tonnes of waste. The annual Indian waste production of the inorganic kind, out of the mining and industrial sectors, has been placed in the range of 290 to 300 Million Tonnes.

Our main mineral or mining-based materials comprise, coal-bitumen combustion residues (mineral ash), coal washery tailings, mine overburden tailings from the various metallic ore mining operations, such as Iron Ore, Copper ore, Lead-zinc Ore, Gold ore and gold minerals and Aluminium industries, including old mine dumps, Red Mud, as well as Old stackings of overburden, particularly around open-cast pits, Old processing centres, now defunct but yet non-rehabilitated. Other products under this category may include Gypsum wastes, Limestone wastes, Lime sludge and marble processing residues, lateritic waste dumps from manganese and bauxite open cats as well as granitic mining wastes/residues including all sizes and shapes of fragments and rock-chips. The well tried materials formed out of these wastes are; special cements, bricks, other construction blocks, tiles, gypsum plasters, fibrous gypsum boards, cement clinkers etc. In case of granite chips and powders, synthetic granite tiles and table-tops and with the limestone/marble wastage materials of this kind glued down to attractive tiles and large wall sheets, have successfully fetched the market.

Mention must be made of some substitution efforts, a really high yielding process like selected high magnesia dunites/peridotites, often wasted from chrome ore mining; substituting for dolomite and magnesite in the conventional iron furnaces. Research is in advanced stage of substituting materials for manganese ore in spiegel making and steel conversion etc., there by reducing the huge manganese ore waste-burdens in many regions. Major electrical substitutions of copper metal by aluminium, has avoided much waste generation of copper mining, an indirect supplemental point in waste to wealth conversion. Lastly the idea of using waste for by-product recovery, becomes compensatory wealth gain from wastes unused otherwise; an example which has yielded economic recovery of nickel and cobalt from chromite ore overburden of the Sukinda area of Jajpur District in Odisha, in the last few years.

Of course an idea of necessary caution will be to adjudge the economicity of efforts of waste to wealth transformation, clearly on a futuristic mind, capable of due projection in perspective planning. However, the waste to wealth researches have to but be continuous.

WASTE TO WEALTH OVERVIEW

During the last three decades, the waste hauling and disposal industry has undergone considerable consolidation. Large consolidators have bought out not only many smaller independent firms but also each other in mega-mergers. The result is an industry with a smaller number of large and vertically-integrated companies, which are less responsive to the needs of communities and smaller recycled-content product manufacturers.

The NGO Institute for Local Self-Reliance [ISLR of USA instituted in 1974] has worked to address these issues since its founding. It was focused not simply on pollution prevention, but also articulated on how communities could increase local capacity and stimulate economic development through the efficient use and reuse of local resources. ILSR's research and analyses identified rules, policies and programmes that could be implemented at the local level to increase recycling and recovery rates and reduce solid waste management costs. It was forecasted that

viable secondary materials economies could be created and sustained at the local level, there by creating (paying) markets for collected recyclables, a new source of income for local governments (particularly public works departments), new enterprises (often established as joint ventures with community organizations), and new training and employment opportunities. The pioneers of a massive "Waste to Wealth" project were drawn from the ISLR on a local and subsequently regional basis. The hypothesis has, with time, proliferated into a viable global concept. Their modest beginnings didn't include the particular role of the Minerals and Mining Industry in any country of the world in the vision, but the missing point is very important as acknowledged by the world now and the same finds prominent inclusion almost everywhere, in considerations of any kind of "Waste to Wealth" project or execution these days. India hardly is any exception.

GLOBAL MINING INDUSTRY

Minerals vary widely in their physical and chemical characteristics. Some are rare, while others are relatively abundant. A typical taxonomy such as that used by United Nations Conference on Trade & Development, divides minerals into metallic, non-metallic and fuel minerals (UNCTAD, 2007: 84). Metals can be further divided into ferrous metals, base metals and precious metals, and non-metallic minerals into construction minerals, industrial minerals and precious stones. While oil and gas are of particular economic importance, the study on the other minerals, including the energy minerals i.e. coal/lignite and uranium/thorium, more than fifty metals, and also a large number of non-metals play a role in the production of the world's economic goods and services and are, therefore, crucial towards today-to-day economic activity as well as social and economic development. The use of minerals and energy has increased dramatically since the industrial revolution, with consumption during the 20th century exceeding the cumulative total of such consumption in all earlier periods. In 2002, the minerals sector accounted for some US$1.2 trillion (about 4 per cent of estimated world GDP). Following dramatic increases in mineral prices starting after 2003, world minerals and energy value added increased to more than US$3 trillion in 2007 (around 6 per cent of world GDP). Oil and gas accounted for about 75 per cent of total mineral production by value, while other minerals (of which coal, iron ore, gold, bauxite, nickel, zinc, copper and the platinum group metals are most prominent) accounted for the remaining share.

From Social-Policy perspective, the distinction between mineral dependent and mineral-rich developing country is important. From a Political-Economic perspective, the mooted query comes on who benefits from mineral wealth and how mineral resources are allocated. As it has been documented in the "resource curse" literature, mineral dependence can be harmful, for instance, when it finances corrupt or authoritarian governments without long-term strategies for economic development, and without redistributing revenues to the population in general and to mining communities in particular. The terms mineral abundance of mineral wealth, on the other hand, suggest that mining can be a source of development — mineral wealth is seen as a positive "endowment" (vide. Doc.Intl.Conf. on Molecular-Based Magnets, 2006). It can therefore produce the financial basis for development, for instance, creating fiscal space to develop a welfare state, as well as financing development, for instance, creating fiscal space to develop a welfare state, as well as financing structural economic and social change. Therefore, the expansion of mineral sectors is planned and managed in a way that enhances the potential macroeconomic benefits and offsets the real or potential damage to host economies, the environment and societies. This broader perspective, which simultaneously explores the macroeconomic, institutional

and sociopolitical effects of mineral development, suggests that the relationship between social policy and mineral wealth needs to be framed in a holistic approach, which takes into account all impacts that mineral wealth produced in a country.

RECYCLING MEANS BUSINESS

Recycling is an economic development tool as well as an environmental tool. Reuse, recycling, and waste reduction offer direct development opportunities for communities. When collected with skill and care, and upgraded with quality in mind, discarded materials are a local resource that can contribute to local revenue, job creation, business expansion and the local economic base.

Recycling-based economic development is the heart of the Waste to Wealth program. On a per-ton basis, sorting and processing recyclables alone is estimated to sustain 10 times more jobs than land-filling or incineration, as established through the experimental work of the ISLR in the USA. However, making new products from the old offers the largest economic pay-off in the recycling loop. New recycling-based manufacturers employ even more people and at higher wages than does sorting recyclables. Some recycling-based paper mills and plastic product manufacturers, for instance, employ on a per-tonne basis, 60 times more workers than do land-fills. Product reuse is even more job-intensive than recycling. It is a knowledge-based industry, with a premium placed on accurate sorting and pricing, and good inventory management.

AN ONGOING PROJECT OF WASTE-WEALTH TRANSFORMATION

The World Bank's Biomass Energy Initiative for Africa (BEIA) through the executive efforts of the American Rescue Team International (ARTI) and with the support of the Ministry of Natural Resources and Tourism (MNRT) is working to build the charcoal briquettes value chain in Tanzania. The goal is to transform the existing charcoal industry from a necessary evil to a rewarding sustainable development opportunity by creating "green" jobs in rural areas.

On a practical level the Waste to Wealth project aims to empower rural inhabitants, especially existing charcoal producers with knowledge, through hands-on practical training on how charcoal can be made from agricultural waste and any other dry biomass which is locally available and free.

RATIONALE & JUSTIFICATION

The rationale and the motivation behind the Waste to Wealth project started in 2006 with the realization that charcoal, however destructive it may be, can never be eliminated from the lives of Africans for the foreseeable future. Hence it was, and still is, pertinent to find reliable ways to mitigate the forest destruction associated with current charcoal production without sacrificing peoples' incomes and livelihoods.

Forests are needlessly cut down for charcoall

The increasing demand by the urban population is enticing the neighbouring rural inhabitants to produce wood charcoal unsustainably for small economic benefits, which comes at a high cost to the forests and the larger ecosystem. This can be reduced and even stopped if the rural dwellers are empowered with the knowledge to produce and supply charcoal in a sustainable method by using agricultural waste and any dry biomass which is plentifully available. The socio-economic benefits of this project alone justify its implementation. The environmental consequences of not promoting such sustainable charcoal makes the project imperative.

Funding

In 2011, field efforts were boosted up with funding through the World Bank's Biomass Energy Initiative for Africa (BEIA) which has allowed us to train 720 people in two Districts and equip them with 120 kilns and 120 manual briquette extruders. In 2012 four Community Based Enterprises (CBEs) are being established with the BEIA funding, linking villages and building the production and sales capacity to complete the charcoal briquettes value chain.

Converting coconut husks into charcoal powder

ARTI acts as the innovation broker developing the charcoal briquette value chain through the Waste to Wealth project. The project first focused at the producer level training and equipping villages to fabricate their own kilns, produce charcoal powder from agricultural waste and other dry biomass and making charcoal briquettes. As villages get trained we link them up into a network of villages to form a community based enterprise, or CBE, focused on briquette production, sensitization and sales. ARTI supports the CBE's with setting up their production process and developing the enterprise skills. Once a CBE has demonstrated its commitment to the production of charcoal briquettes ARTI supports them with an electrical briquette extruder(s) on loan, which the CBE pays back with briquettes

Sifting the charcoal powder

In 2012, full scale process has been initiated more on supporting the CBE's in branding, marketing and creating sales networks for their briquettes, thus manufactured.

The Technology Involved

The technology originated from ARTI-India, a research and technology institute based in Pune, India. With the blessing of ARTI-India, ARTI-TZ adopted the technology seeing the huge potential for its commercial application in Tanzania.

The kilns we use to produce the charcoal powder are made from used oil drums. Initially larger kilns were used, that required 9 drums to produce. Changes have since been initiated in the type of kiln used to a smaller one that requires only 2 oil drums to fabricate, which is much cheaper and produces charcoal powder more efficiently. We are constantly trying to improve on the kiln design to have good quality charcoal powder but also at a reasonable cost.

CBEs use larger, electric, extruders

In order to produce the briquettes it became necessary to modify manual and electrical meat mincers. They have proven to be a cost effective way to produce quality charcoal briquettes with a simple technology.

How has the community benefited

While the Waste to Wealth project is still at the pilot stage it is already proving to be a viable alternative to wood charcoal and a great benefit to communities. People no longer have to go to the forest to cut trees for charcoal. They can earn an income from an activity that is not environmentally destructive. The District Forest Officers, who are responsible for issuing permits to cut trees for charcoal production, have provided incredible support in terms of time, knowledge and working space.

50% of the producers are women

This support comes from the fact that in the past they had no choice but to issue permits as there was no alternative to wood charcoal. Charcoal briquettes offers that alternatives. Women have also started to benefit from the charcoal briquette trade, as production can be carried out closer to home and in conjunction with other agricultural activities. Unlike the traditional charcoal trade, charcoal

briquette enterprises are proving to be more gender balanced.

Challenges & Opportunities for expansion

The Waste to Wealth project is currently in the pilot stage and the charcoal briquettes supply does not even represent 0.05% of the estimated 650 million USD trade in charcoal annually in Tanzania. In order to reach 1% or even 10% of this industry we must invest heavily in training and equipping rural producers as well as generated market demand for charcoal briquettes, through sensitization campaigns and the overall development of the value change. Work also needs to be done on created the policies and incentives to help facilitate the transition from wood charcoal to charcoal briquettes.

Some Other Waste-Wealth

Transformation Projects in Operation

Living Earth Foundation (UK) and its partners Living Earth Uganda and Fondation Camerounaise de la Terre Vivante are working with urban slum dwellers, entrepreneurs and local government **in** Douala (Cameroon), Port Harcourt (Nigeria) and Kampala (Uganda) on a '*Waste to Wealth*' project. This three year project aims to enable these groups to take the lead in improving living conditions and livelihoods in their cities through the establishment of micro level public-private partnerships for service delivery, and the promotion of income generating 'waste to wealth' activities.

In fact, there are numerous other small and medium sized projects currently run in many countries of the world, aiming to convert waste to wealth, in a simpler and sustainable way and most of them with positive cost-benefit advantages as well.

Over Exploitation of Mineral Resources

How much of minerals and ores, we really need immediately, allowing some small largesse for near future? In the entire history of human civilization such an unusually high demand has never been placed on natural resources of our planet. The consequences of this over-exploitation of mineral wealth have to be serious, drastic and enormously damaging to the entire biosphere. These can be summed up as follows:

1. Rapid Depletion of High Grade Mineral Deposits

Exploitation of mineral wealth at a rapid rate shall naturally deplete our good quality deposits. The ever rising demands shall compel miners to carry on the extraction from increasingly lower and lower grade of deposits which possess a poorer percentage of the metal. For example copper was extracted from ores containing 8-10% of metal content about 500 years ago.

Now we are using deposits which contain only 0.35% of copper. To produce one ton of copper metal we have to dig out 285 tons of ore. This shall naturally involve a large amount of energy expenditure as well as a large quantity of waste material production.

We may never reach an end as matter is indestructible. Most of the metals we require are present in highly dispersed state in the soil, the rocks and the trash or wastes we discard. With a sophisticated technology we can fulfill most of our requirements from these sources, But the overall cost could be heavy, causing the metals to become more and more costly.

2. Wastage and Dissemination of Mineral Wealth

Most of our mineral deposits occur as a complex mixture of a number of mineral elements. After removal of top soil and rocks we dig out the desired mineral leaving behind others which are often left in the open as waste materials. Extraction of one element usually scatters and wastes a number of other elements, many of which are in short supply.

This wastage rises as more and more ores are extracted and processed. Worldwide smelting of minerals for extraction of metals introduces an enormous quantity of sulphur, heavy metals such as mercury, cadmium, nickel, arsenic, zinc etc. into the environment which are separately mined elsewhere.

We are technologically competent enough to extract these metals from the wastes produced from one mining industry rather than excavating fresh deposits. The cost could be heavier indeed but the practice shall pay in the long run. It will conserve our resources and also reduce the burden of pollutants which we have to introduce in the environment.

3. Pollution of Environment from Mining and Processing Wastes

Mining is a dirty industry. It has created some of the largest 'Environmental disaster' zones in the world. The mining and processing of minerals generally involves following steps:

a. The soil and rock overlying the mineral deposits, called the 'over-burden' in miner's language, has to be removed before actual mining operations commence.
b. The ore is then mined and crushed.
c. After being converted to fine powdered state it is run through concentrators which remove impurities.
d. The concentrated ores are then reduced to crude metal often at a high temperature by various methods depending upon the chemical nature of the ore.
e. Crude metal is then refined or purified in refineries.

Each step in mining and processing operations produces large quantities of waste materials. As most of today's mines are simple surface excavations, the first task of a miner is to remove whatever lies over the mineral deposit, be it a mountain, a forest or an agricultural field. Under-ground mining with a system of shaft and tunnels does not produce as much waste as open cast mining does. In 1988, over-burden, the material overlying the mineral deposits in U.S. A., amounted to about 3.3 billion tons of matter moved. This material even if chemically inert, clogs streams, gets deposited in lakes and clouds the air over large areas. If it contains sulphur and other reactive elements apart from wastage of our precious resource a number of other problems are caused. Almost similar problems arise from the disposal of waste material produced after concentration of an ore. This material is called 'tailings' in the miner's language. As most of the ores contain a large amount of sulphur its oxidation and leaching results in formation of acidic leachates (Water containing dilute sulphuric acid).

The finely grounded state of ores makes metal contaminants which were earlier bound in solid rocks, available to acidic waters. Thus, these leachates contain appreciable amounts of heavy metals and toxic trace elements. Tailings may contain residue of organic chemicals such as toluene etc. which cause another type of problems. Ponds full of acidic leachates covering thousands of hectares of land surface now surround copper mines in U.S.A. These waters cause serious problems of water pollution if they happen to contaminate our surface or underground acquifers.

The grade of ore is important in determining the overall impact of mining activity. An ore containing 20% of metal content shall produce only four tons of tailings or waste material per ton of metal extracted but a low grade ore containing 1% of metal shall produce 99 tons of tailings per ton of metal obtained. Gold mining is particularly damaging in this respect as the metal content of gold deposits is at best expressed as parts per million. Miners at Gold Strike mine in Nevada - the largest in USA move about 3, 25,000 tons of ore to produce about 50 kg of gold per year. In Amazon basin, Brazil, miners use a technique called hydraulic mining which involves blasting the gold bearing hillside with high pressure stream

of water following by guiding the sediments through ducts where the gold being heavier settles down from tons of non-valuable material.

This silt and sediments are finally washed down into some local stream. The practice has silted local rivers and lakes while the use of mercury to trap gold from sediments has contaminated large areas. Miners release an estimated 100 tonnes of mercury into the waters of the River Amazon annually. In North America, miners use 'Heap Leaching' a technique which allows gold extraction from a very low grade ore. The technique involves sprinkling of Cyanide solution over a heap of low grade ore. While trickling down the solution dissolves gold. It is collected and later gold is recovered from it. Both cyanide solution reservoirs and contaminated tailings are left behind after the gold extraction.

These pose hazards to wild life and threaten surface waters as well as under-ground acquifers. In October 1990 about 45 million litres of cyanide solution from a reservoir at Brewer Gold Mine, South Carolina, spilled over into a tributary of local Lynch River, killing more than 10,000 fishes. Thousands of birds die each year when they mistakenly consume Cyanide solution from these impoundments.

4. Pollution Caused by Heavy Energy Requirement of Mining Industry

Moving huge amounts of sand silt and clay etc. requires energy. Concentration of ore requires energy. Smelting and refining operations require energy. Electrolytic processes used for refining of some metals, like Aluminium, require energy.

Disposal of solid or liquid wastes or tailings requires energy. Transportation of solid or liquid wastes or tailings requires energy. Transportation of finished products requires energy. The overall worldwide requirement of energy in mining industry adds up to an enormous amount. This energy comes from diverse sources which mostly include fire-wood, coal, petroleum, natural gas and electricity. In order to provide energy to mining industry a huge quantity of these materials are burned which causes a variety of pollution problems.

Global Waste generation Scenario

Globally estimated waste production for 2010 was around 20 Billion Tonnes comprising the sum total of organic, inorganic, hazardous and nonhazardous, industrial, mining-metallurgical, municipal and other miscellaneous rejections. Asia alone was responsible for 4.4 Billion Tonnes and out of that, China shared 1.2 Billion Tonnes while India owned up the gross tonnage of a Billion Tonnes of waste. The annual mining and industrial inorganic wastes for India has been placed ad 290 Million Tonnes, of which the contribution from Mineral sector exclusively is visualized as 100 to 120 Million Tonnes.

Indian Waste generation Scenario: Recycling & Utilization

In the Indian context, our main mineral or mining-based materials comprise, coal-bitumen combustion residues (mineral ash), coal washery tailings, mine overburden tailings from the various metallic ore mining operations, such as Iron Ore, Copper ore, Lead-zinc Ore, Gold ore and gold minerals and Aluminium industries, including old mine dumps, Red Mud, as well as Old stacking sites for overburden, particularly around open-cast pits, old processing centres, now defunct but yet non-rehabilitated. Other products under this category may include Gypsum wastes, Limestone wastes, Lime sludge and marble processing residues as well as granitic mining wastes/residues including dusts.

The well tried materials formed out of these wastes are cements, bricks, other construction blocks, tiles, gypsum plasters, fibrous gypsum boards, bricks, blocks, cement clinkers and in case of granite chips and powders, synthetic granite tiles.

Mention must be made of some substitution efforts, a really high yielding process like selected magnesium-rich dunites/peridotites, often wasted from chrome ore mining; substituting for dolomite and magnesite in the conventional iron furnaces. Research is in advanced stage of substituting materials for manganese ore in Spiegel making and steel conversion etc., there by reducing the huge manganese ore waste-burdens in many regions. Major electrical substitutions of copper metal by aluminium, has avoided much waste generation of copper mining, an indirect supplemental point in waste to wealth conversion. Lastly the idea of using waste for by-product recovery, becomes compensatory wealth gain from wastes unused otherwise; an example which has yielded economic recovery of nickel and cobalt from chromite ore overburden of the Sukinda area in Odisha in last few years.

Of course an idea of necessary caution will be to adjudge the economicity of efforts of waste to wealth transformation, clearly on a futuristic mind, capable of due projection in perspective planning.

CONCLUSION

It is needless to mention that a lot more research and sustained efforts are warranted for establishing standardized utilitarian procedures and services in all fields, including mineral industry and mining sectors, where optimization in India is far below the requirements and expectations. R & D efforts towards "waste to wealth" goal must remain steady and continuous. The investment made now shall give back huge returns in the long run.

The brief case history of a total project carried out in Tanzania, well into the present viz.2012 presented elsewhere, can serve as a kind of checklist towards the management needs, such as motivation, funding, organization of supply and demands of raw inputs as well as finished products into the market as well as satisfying social demands, a must for any similar efforts on moderately wide scale. An aim of making a programme for Zero Waste must envisage a few concrete steps of management as indoctrinated by Robin Murray(1999), of which the concrete points importance are summarized, as under:

1. The economic playing field must be rebalanced. The hierarchy of profitability must match the environmental hierarchy. This can be done by revising waste taxes and public benefits in three ways:

    - o introducing a disposal tax that reflects the environmental hierarchy
    - o cutting the subsidies presently given to incineration
    - o introducing a price guarantee scheme for recycled materials to fund the build-up costs of four stream recycling.

2. The £550 million raised in waste taxes must be re-channelled to a Zero Waste Fund, which requires:

    - o a change in the landfill tax regulations so that the 20 per cent offsets are paid into public-run Recycling Fund.
    - o earmarking a further 20 per cent to support employment and environmental goals through recycling
    - o amending the packaging recovery regulations so that payments by the 'obligated parties' are channelled to recycling collectors

3. Establishing a Zero Waste Agency to administer the transitional funds and 'animate' the change.

4. Founding a new type of Green Academy, equivalent to the German technical schools of the mid-nineteenth century. It would be charged with developing organisational forms, knowledge and skills relevant to zero waste, and new

ways of generating 'distributed intelligence'. Its curricula and priorities would be set by the needs thrown up by the new environmental systems. Hence its research, teaching and skill formation would be linked closely to ground level projects - following the approach of the Ulm School of Design - and provide learning resources to those in or outside employment.

5. Appointing Zero Waste Advisers - some recruited from leading recycling and reduction projects overseas - to advise on recycling schemes and projects. The group would be part of an international network, promoting exchanges and part-time attachments, and linking into practitioners' associations.

6. The launch of a 'Closed Loop Industrialisation' Initiative, promoting the development of secondary materials industries, ecodesign and hazard reduction technologies. In addition to material productivity, it would aim to promote 'de-scaling' technologies suitable for local and regional economies. It would be organised in conjunction with regional development agencies.

7. The extension of producer responsibility into new fields, not only electrical and electronics appliances, end-of-life vehicles and tyres, but other durable equipment, newspapers, and hazardous products and materials. The weight of responsibility should be placed at the point of product and process design, since they have the greatest capacity to develop alternatives. In each case, the finance contributed by producers should be re-channelled to develop the alternatives.

8. **Devolving responsibility for waste disposal to districts**, through direct payments for the costs of disposal (rather than property-based precepts) and giving districts responsibility for identifying and negotiating disposal options within their own boundaries or with neighbouring districts. This would represent the proximity principle with teeth.

9. **Restoring public confidence in wade management and democratising risk** through: planning reform to give financial support and access to information to civil groups and neighbourhoods affected by waste proposals; a new culture of openness in regulatory bodies; an independent waste hazards control advisory body; and an environmental freedom of information provision.

10. **A government-led commitment to the zero waste target 'within a generation'**, reflected in the above measures and the adoption of tighter targets to 'reduce with the aim of eliminating' mixed waste disposal by 2010. This would include a phased ban on organic waste in land-fills and on land-filling or incinerating hazard-producing materials, and a moratorium of new mixed waste incinerators for five years.

The method suggested is, by no means, claimed to be the only method or the very best method. The primary objective of its presentation is to encourage the formulation of foolproof checklists, for perfect use as a matter of technique, in projects initiated with a "Waste to Wealth" doctrine in purview.

REFERENCES

Asokan Pappu, Mohini Saxena, and Shyam V.Ashtekar 2007: Solid Waste generation in India and Recycling potential, Bldg & Environ.,42(6), 2311-2320.

Asokan Pappu, Mohini Saxena, and Shyam V.Ashtekar 2011: Waste to Wealth – Recycling opportunities & Challenges, 23(2), March Issue, 14-23.

Debjani 13th Feb.2012 Over Exploitation of the Mineral Resources, Google Artic.

Deirdre Grace [Seattle:Clean Washington] 1992: Recycling is Working, Open file report, November Issue.

L.Hindojosa, A.Babbington, A.Barrientos, and T.Addison 2010 UNRIS Social Policy & Dvpt Paper 44, September Issue.

Robin F.Ingenthron 1992 Value added by Recycling Industries in Massachusetts, USA,[Boston : Department. of Environtal Protection], July Issue.

Robin Murray 1999 Creating Wealth from Waste, Book Chapter 14 Excerpts, Demos & Ecologika Publcn, "Programme for Zero Waste".

*Instt. of Local Self-Reliance, Minnesota www.islr.org/initiatives/**Waste to Wealth/***

*American Rescue Team International www.arti-africa.org/projects/**Waste to Wealth/***

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CONVERSION OF SOLID WASTE FINES OF COMMINUTION PROCESS INTO FEEDING MATERIAL OF THE BLAST FURNACE GRADE IRON ORE PELLETS

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ABSTRACT

For the production of suitable sized feed materials (-40+15mm) for Blast Furnace, during comminution process (crushing, grinding and screening) of the Run of Mines (ROM) generates a lot of fines (-15mm) almost 50% of the total output. These waste fines are being utilized as converting into Sponge Iron, Sinter, Briquettes and Pellets. For making pellets the size of the fines should be below 100 micron. The particles smaller than 3 mm generated are commonly termed as "Waste Fines". The quantity of these fines amounting nearly 50% of the total waste iron ore and lime stone fines. The disposal of solid waste fines cost money, render material loss and posses many environmental issues. The conversion of solid waste fines into value added products for use is the policy of the day.

The present study deals with the utilization of these fines (-3mm) to convert into value added products i.e. Fluxed pellets which could be used as a feed material to control lime stone addition as well as smooth operation of the blast furnace. The study comprises to understand the physical (apparent and true porosity, microstructure) and mechanical behavior (Shatter, tumbler, abrasion, and crushing strength) of hardened pellets. The crushing strength and true porosity of hardened acid, neutral and basic pellets were found as 42.5Kg, 35.0Kg, 48.33 Kg & 50.54%, 45.64%, 45.47 % respectively at 1200°C . On the other hand, higher crushing strength (Acid-233Kg, Neutral-486Kg, Basic-586Kg) was observed at 1300°C due to fused slag, which was visualized on SEM-EDAX, resulting low porosity (8.5%) as similar to lump ore (8.2%).

The shatter, tumbler and abrasion resistance of hardened pellets were also examined and compared with lump ore. It was found that at 1300°C Shatter, tumbler, and abrasion resistance were found 100, 99.8 & 0.2(acid), 100,100 &0 (neutral), 100, 100& 0(basic) against 94.4, 90.2 & 6.7 (lump ore).

From the present study it was concluded that, the property of acid pellets was better than lump ore and found superior property in fluxed pellets than acid pellets which could be used as a feed material in the Blast Furnace.

Key Words: *waste fines, fluxed pellets, agglomeration, porosity of pellets*

1. INTRODUCTION

Steel is used in all sector of the society including domestic equipments, agricultural tools, transport system, defense armaments, space vehicle etc. India is the 4th largest steel producer in the world. India produced 65.1 million tons of crude steel upto the month of October, 2012 where world steel production was 1261.45 million tons (fig.1) against 72.7 million tons of steel in the year of 2011 where world produced 1527 million tons of steel (Crude steel Production, 2012). It is being expected that Indian steel production will grow 10% during 2010-2013. (Indian Steel Market watch, 2011). World Blast Furnace Iron (BFI) Production upto the month of Oct, 2012 was total 913.82MT by 38 countries in which India produced 36.2 million tons occupying also 4th position in the world whereas World Direct Reduced Iron (DRI) Production upto the month of Oct, 2012 was total 45.30MT by 11 countries in which India produced 17.85 million tons occupying 1st position (fig. 2).

The production of 1tonne steel is obtained by using nearly 1.5tonne of iron ore, 2.5tonne coal (Coking & Non Coking), and 0.5tonne limestone as raw materials. These raw materials from the mines are subjected to Mineral Beneficiation Operation

(Crushing, Grinding, Sizing, Washing etc.) for making suitable feed for Iron Making.

According to Indian Bureau Of Mines, Nagpur ,the total output of 208 million tones of ROM in which, lump iron ore constituted 82.2 million tones or about 39.5%, fines 125.1 million tones or about 60.2% and concentrates 0.7 million tones or about 0.3% of the total output of iron ore lumps.(Indian Minerals Yearbook 2011), 20% of total coal mined and 22.5 % quarry fines of lime stone(Quarry fines are those fines generated by processes related to blasting, processing, handling and transportation) i.e almost 50% of total lime made(UK Minerals Yearbook, 2006). The particles, smaller than 3 mm size, are generated commonly termed as "Waste Fines".These fines are partially utilized in the processes like Pellet Making, Power Plant, Desulphurization respectively. The disposal of these solid waste fines adds the cost, render material loss and posses many environmental issues. The conversion of solid waste fines into value added products for use is the policy of the day.

In conventional method, Lime Stone and Dolomite in bulk are being used as flux inside the blast furnace. The main problem of adding these as a flux is loading alkali inside the furnace. The alkali cycle inside the Blast Furnace is maintained in between 900°C-1100°C (Biswas, 1981). This problem could be minimized by using hardened fluxed iron ore pellets because during hardening (>1100°C) operation of the fluxed pellets, alkali (Na_2O, K_2O) got evaporated. Since the last 3 decades, fluxed iron ore pellets have been slowly taking over the load of acid pellets as the primary burden around the world. In fluxed pellets, limestone and dolomite are added to the magnetite or hematite concentrate, which already contains silica as a gangue. One of the primary strength forming mechanisms in iron ore pellets is the formation of liquid bridges between the iron oxide particles at high temperature. Adding of lime to iron ore pellets changes the chemistry of these liquid bridges from iron silicates to iron calcium silicates. (Firth.et al, 2008).

In the present study we made the fluxed iron ore pellets from solid waste fines of iron ore and lime with the required proportion to get the different composition of pellets. It was tested for its physical and mechanical properties and it was compared with the property of lumpy iron ore. It was also compared with the different types of pellets made.

2. EXPERIMENTAL

2.1. Materials Selection

In the present investigation, solid waste iron ore fines (-3mm) from Orissa (Barbil area) and limestone fines (-3mm) from Rajasthan mines (Figure 3a and 3b) were used.

2.2. Chemical Composition

Chemical Analyses of iron ore and lime stone were shown in table-1

2.3. Determination of Phase in the Raw Materials

XRD analysis (Model no. Rigaku D-MAX IIIB) of iron ore and lime fines were done under following conditions: emission radiation=CuKα, voltage=40 kV, intensity=30 mA, with a scan rate of 2° /m. XRD Spectra were shown in Figures 4 and 5 respectively. Different phases present in the iron ore and lime fines (-72 mesh) were determined by JCPDS software and calculated the weight percentage of Fe_3O_4, $Ca(OH)_2$ etc

2.4. Preparation of Iron Ore Pellets with Varying Lime Fines

Preparation of fluxed pellets are done as per flow chart as shown in Figure 6.

2.4.1 Calcinations of lime stone

Limestone samples were heated at 1050 °C @5°C/minute in a laboratory type muffle furnace and kept for isothermal holding for a period of one hour and then furnace cooling done to get burnt lime.

2.4.2 Grinding:

Burnt lime and iron ore samples were ground separately in a lal ›ratory ball mill of 5 kg capacity and all sample screened through BS-72 mesh (0.2mm) sieve respectively.

2.4.3 Pellets making

Pellets (size: 18mm approximate dia.) were made by prolonged hand rolling of moistened iron ore fines of -72mesh size, with adding 0%, 2%, 4% lime powder to get acid (Basicity 0), neutral (Basicity ≈1) and basic (Basicity ≈2) respectively without bentonite. The disadvantages of unwanted impurities by using bentonite were discussed in several studies. For instance, the addition of 1% bentonite, containing 85% SiO2+Al2O3, decreases the pellet's iron content to 0.6% (De Souza et al, 1984). Properties of different types of green iron ore pellets were given in Table 2.

2.5 Testing Of Green Pellets

Green pellets of around 18 mm size were tested for crushing strength with the help of a 'Green crushing strength measurement setup' as shown in Figure 7. Drop strength was measured by dropping the pellets at a height of 450 mm over a steel surface until break. The values were given in Table 3.

2.6 Curing and Hardening

The green pellets were air dried for two days to get surface moisture free and sufficient strength for further treatment. Three pellets of each composition were taken out for testing purpose. Rest pellets were dried at 110°C for 2 hrs in an oven and similarly 3 pellets of each composition taken out for testing purpose. Then rest pellets were hardened in a resistance furnace at different temperature of 1100°C, 1200°C and 1300°C for 1 hour to attain a workable strength as per heating cycle mention in the Figure 8. Figure 9 shows the colour changes of different types of pellets after hardening. These hardened pellets were then kept in desiccators for its characterization (i.e. porosity, specific gravity, crushing strength and microstructure)

2.7. Testing of Dried and Hardened Pellets

2.7.1 Strength measurement of dried pellets

The Crushing strength of three samples of each air dried, oven dried (moisture removed) and hardened pellets were tested under compressive load in a low range UTM (SHIMADZU Type: SBL, P/N: 340-43120-01, Capasity-5kN) at a very slow speed of 0.05cm/minute. Results were given in Table 4 and figure 10.

2.7.2 Porosity measurement of hardened pellets

Porosity of three types of pellets at different hardening temperature were examined by both 'kerosene' and 'Hot Test Boiling Water method'(HTBW) (Chesters, 1973). The kerosene method as per IS standards(IS: 1528,part-VIII-1974) as adopted to estimate the porosity of the materials including meso pores which we could not estimate in HTBW due to high viscosity and low wettability of water. The results of density and porosity of pellets were given in Table 5 and Figure 11, along with lump iron ore for comparison.

2.7.3 Mechanical property determination

500 Grams (Non standard weight basis) of hardened pellets were taken to measure, as per (ISO 3271:2007) Tumbler, Abrasion (figure 12) and Shatter test (figure 13) to get

the ideas in the variations of the properties in between and along with lump iron ore as given in table 6 and figure 14.

2.7.4 SEM-EDAX analysis of hardened pellets

Hardened pellets were cut into two halves and examined through SEM-EDAX analyzer (FEI Quanta-200FEG) at 20kv on scan rate 10μs with ETD detector for knowing the different phases present inside the pellets as shown in Figure 15.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Raw Materials

1. Qualities of burden materials affect the economy, output, and efficiency of the furnace operation. The chemical analysis of iron ores and lime stone under investigation were listed in Table 1.The value of iron content in the iron ore was 64% and 52% CaO in Lime Stone. Data for the mineralogical composition indicated that the gangue materials in the iron ore mainly alumina and silica with a negligible amount of MgO, Mn, P, S and alkali.

2. The XRD analysis (Figure 4) reveals that % Fe_2O_3 in iron ore was around 95%. It means that iron ore was as hematite and soft in nature. Next XRD analysis (Figure 5) was indicated the different phases present in burnt lime. $CaCO_3$ was observed very less in quantity (i.e. <5). It could be concluded that the burnt lime has only CaO.

3.2. Physical and Mechanical Properties

3.2.1 Fracture behavior of green pellets

During crushing strength measurement of green pellets it was observed that in acid pellets crack initiates and propagate slowly until fracture. But increasing lime content it was observed that crack initiates and propagate instantly and fracture occurred without warning. It means that increasing lime content decreases the plasticity and fractured like brittle behavior. The SEM micrograph of lime fines particle reveals that the acicular needle like structure of the lime fines particles (figure 3c) were responsible for that.

3.2.2 Strength

From the result it was observed that the green crushing strength of pellets were decreased with increasing lime content because of decreasing its plasticity. But increasing lime content, the calcium hydroxide of the pellet reacts with environmental CO_2 and formed hard $CaCO_3$ which increased its content on the surface of the green pellet which enhanced the strength (Patil et al.,1980) (Table 3). Crushing strength was increased for air dried, oven dried and hardened samples (Table 4 and Figure 10). Increasing hardening temperature crushing strength also increased. But the remarkable changes occurred at hardening temperature of 1300°C. After increasing temperature of 100°C, crushing strength was increased 10 times of hardening temperature of 1200°C. There were no considerable changes of hardening at 1100°C and1200°C, with comparison to Lump ore sample.

Another three important mechanical properties of ore were shown in table 6 and figure 14. With increasing hardening temperature and lime content, Shatter Strength, Tumbler Strength and Abrasion resistance were increased. But only hardening temperature 1300°C shows the superior quality than the lump ore.

3.2.3 Porosity

In the temperature range of 1100°C to 1200°C, apparent porosity value of iron ore pellets were 41.78%, 51.48%, 57.58% and 44.67%, 46.69%, 47.71% respectively for acidic, neutral and basic pellets as shown in table No 5 and figure 11. In 1300°C hardening temperature, apparent porosity was decreased to 33.89%, 21.71% and 8.5% for acidic, neutral and basic pellets

respectively. But it was not decreased for basic pellets upto the value of lump ore (8.1%). The nature of trend for true porosity was found similar to the apparent porosity. With increasing % Lime, porosity was increased for the temperature range of 1100°C to 1200°C. But reverse effect shown for hardening temperature 1300°C (figure 16) because at that temperature, slag fused and goes inside the pores of the pellets, hence it caused the lower porosity but increased % of sealed porosity. This is the reason for increasing strength for 1300°C hardening pellets (Wynnyckyj & Fahidy, 1974) and (Hamilton, 1976). Porosity of materials is responsible for accelerating the reduction behavior which decreases the coke rate in the Blast Furnace. On the other hand, strength of the material has capability to bear load of burden inside the working condition of Blast Furnace.

3.2.4 Fusion behavior and colour changes

After hardening, colour change of the pellets was observed as shown in figure 9. It was observed that with increasing % lime addition, the colour of the pellets were changed from Brownish to whitish with increasing hardening temperature and finally become blackish at 1300°C due to fusion and agglomeration. With increasing lime content, fusion characteristics were increased subsequently and formed stronger bonds between particles of the pellets.

3.2.5 Phase analysis

SEM images of hardened pellets were shown in Figure 15. In lower hardening temperature more porosity and free particles were observed resulting lower strength although after hardening. But at 1300°C hardening temperature particles were fused and agglomerated resulting less porosity but higher strength which was also observed physically illustrated in Sec. 3.2.4. From the ternary diagram of CaO-Fe_2O_3-SiO_2 (Figure 18), it is clearly shown that low melting phases produced at a low melting temperature of near about 1200°C. In Figure 15 it was clearly shown that at high hardening temperature Slag Bridge (main responsible for hardening strength) tightly bonded to get the strength. It was seen in SEM-EDAX with increasing lime content, silicate slag phase transformed to calcium silicate phase, which will generate higher strength as shown in figure 17. It was also discuss by other author (Panigrahi et al, 1990). So these are the reasons for producing low melting phases in basic pellets than acid one, which creates more fusion behavior, more strong slag bonds, resulting high strength and lower porosity.

4. CONCLUSION

Following conclusions were drawn with reference to the Blast Furnace burden.

1. Huge amount of lime and iron ore fines generated from mines can be utilized for making fluxed pellets
2. Fluxed pellets have superior property than acid pellets as well as lump ore.
3. Lime use inside the flux pellets minimize the problem of use lime stone concentrate.
4. Increasing hardening temperature porosity value increases tremendously (upto 51%) at a temperature below 1300°C. At 1300°C, slag inside the pellets fused resulting less porosity (upto34%) and enhances crushing strength (586 kg/pellet) as compared to lumpy ore (400-700 Kg/cm^2)
5. Apparent and true porosity were improved in comparison with lump iron ore and its pellets.
6. Shatter and tumbler strength were found better at hardening temperature of 1300°C compared with lumpy iron ore.
7. In basic pellets due to CaO presence, more low melting phases formed than acid pellets resulting more fusion behavior, stronger slag bond, resulting higher strength and mechanical property as well as lower porosity value.

5. ACKNOWLEDGEMENTS

Authors are thankful to Prof. R. C. Gupta, former Head of the department, Met-Engg. IIT (BHU)-Varanasi, for his encouragement and valuable suggestions in these aspects. We are also thankful to the Heads of the department, Met Engg., IIT (BHU), for completion of this work.

6. *REFERENCES*

Biswas A K, 1981, Principles of Blast Furnace Iron Making, SBA publication, Kolkata, pp-499

Chesters, J. H., 1973, Refractories: Production and Properties, London: The Iron and Steel Institute. pp. 472.

Crude steel Production, 2012, (available at http://www.worldsteel.org/statistics/crude-steel-production.html)

De Souza, R.P., De Mendonca, C.F., Kater, T., 1984. Production of acid iron ore pellet for direct reduction using an organic binder. Mining Eng. Magn. 36–10, pp.1437–1441.

Firth. A.R., Garden.J.F., Douglas.J.D., 2008,Phase Equilibria and Slag Formation in the Magnetite Core of Fluxed Iron Ore Pellets, ISIJ International, Vol. 48 (2008), No. 11, pp. 1485–1492

Gupta. R.C., 2010 ,Theory. and Lab. Exp. in Ferrous Metallurgy, PHI publication, New Delhi, pp.70-77

Hamilton, J.D.G., 1976, Mechanisms of bond development in hematite iron ore pellet fluxed with limestone. Trans. Inst. Min. Metall. Sc. C 85 (3), 30–39.

Indian Minerals Yearbook 2011, (Part-II),50th Edition, IRON ORE, (ADVANCE RELEASE),GOI, MINISTRY OF MINES ,INDIAN BUREAU OF MINES, NAGPUR (available at http://ibm.nic.in/IMYB%202011_Iron%20ore.pdf).

Indian Standard (IS: 1528,part-VIII-1974],Methods of Sampling and Physical Tests for Refractory Materials - Part VIII : Determination of Apparent Porosity

Indian Steel Market watch, 2011(available at http://mjunction.in/ marketnews/metals/ india_fy11_ steel_production_at.php).

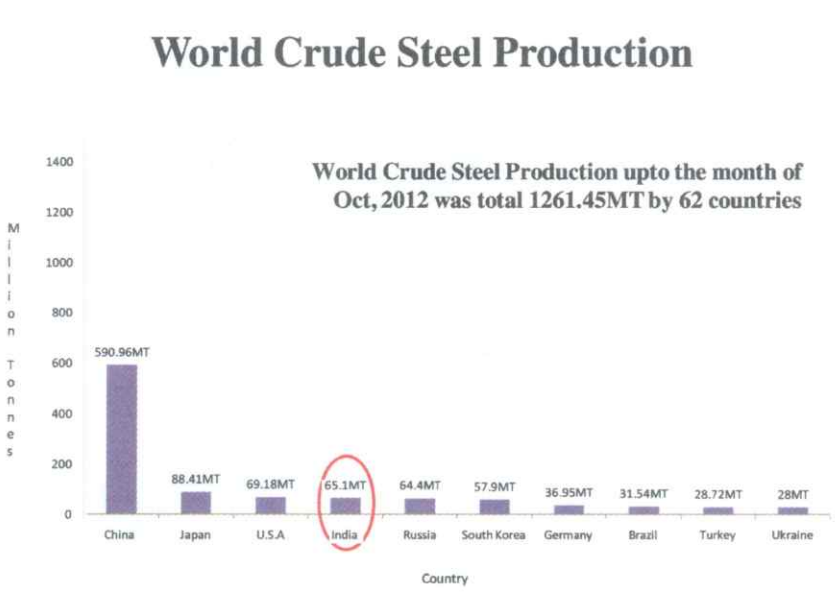
ISO 3271:2007, Iron ores for blast furnace and direct reduction feedstocks determination of the tumble and abrasion indices.

Panigrahi, S.C., Jena, B.C., Rigaud, M., 1990. Characterization of bonding and crystalline phases in fluxed pellets using peat moss and bentonite as binders. Metall. Trans. B 21, 463–474.

Patil, J. B., Kakkar, N. K., Srinivasan, T. M., Dharanipalan, S., Patel, B. B., and Nayak, N. M., 1980, "Production of cold bonded pellets." Transactions of the Indian Institute of Metals, 33(5), pp. 382–390.

UK Minerals Yearbook, 2006, lime stone (available at www.mineralsuk.com/ britmin/ ukmy2006.pdf)

Wynnyckyj, J.R., Fahidy, T.Z., 1974. Solid state sintering in the induration of iron ore pellets. Metall. Trans. 5, 991–1000.



Source:- www.worldsteel.org

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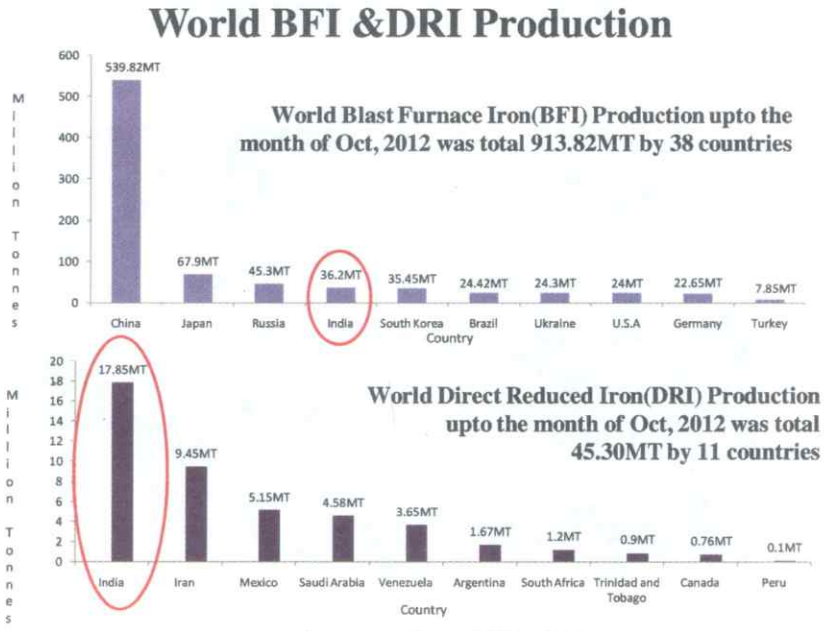
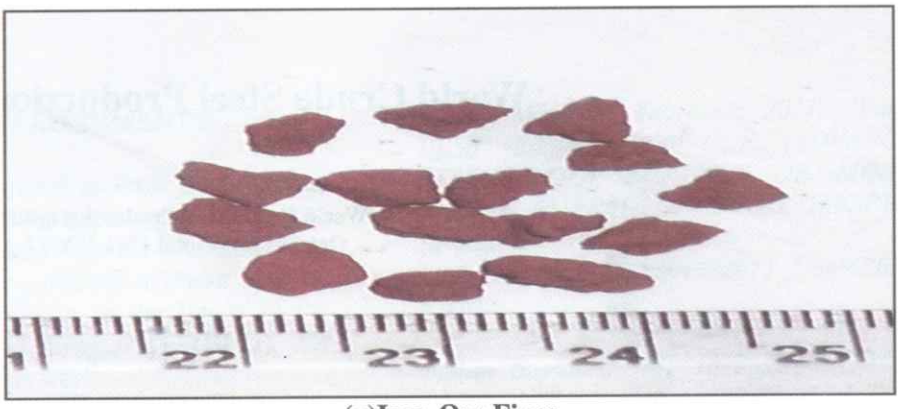
Figure No.1: World crude steel production



Source:- www.worldsteel.org

Figure No. 2: World BFI and DRI production



(a)Iron Ore Fines

(b)Lime Stone Fines

(c) SEM micrograph of Lime fines

Figure 3: Photographs of Raw Materials used in present study

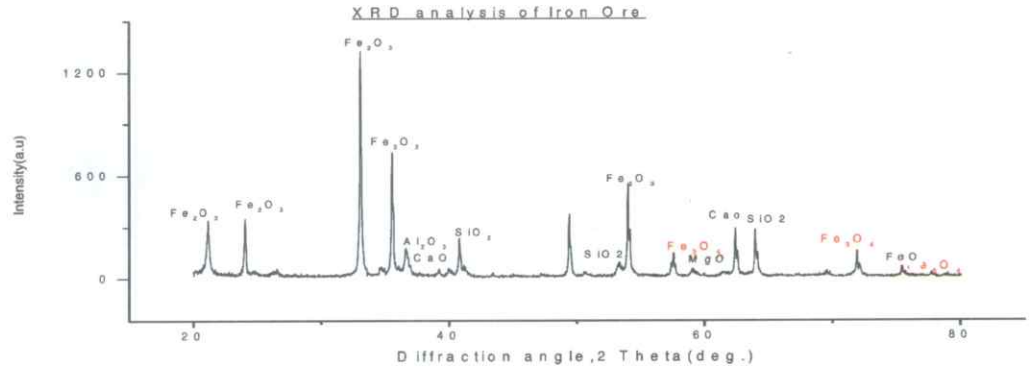


Figure 4: XRD Pattern of Iron ore

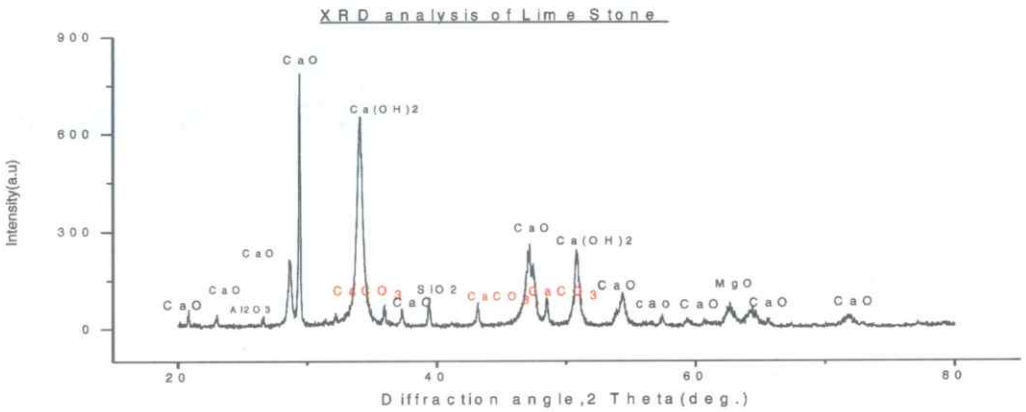


Figure 5: XRD Pattern of Lime Fines

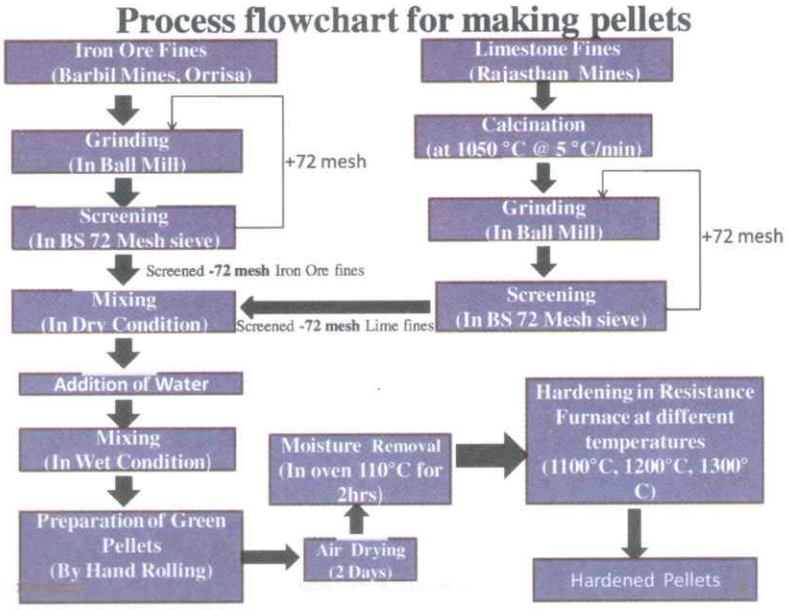


Figure No. 6: Process flow chart of preparation of pellets

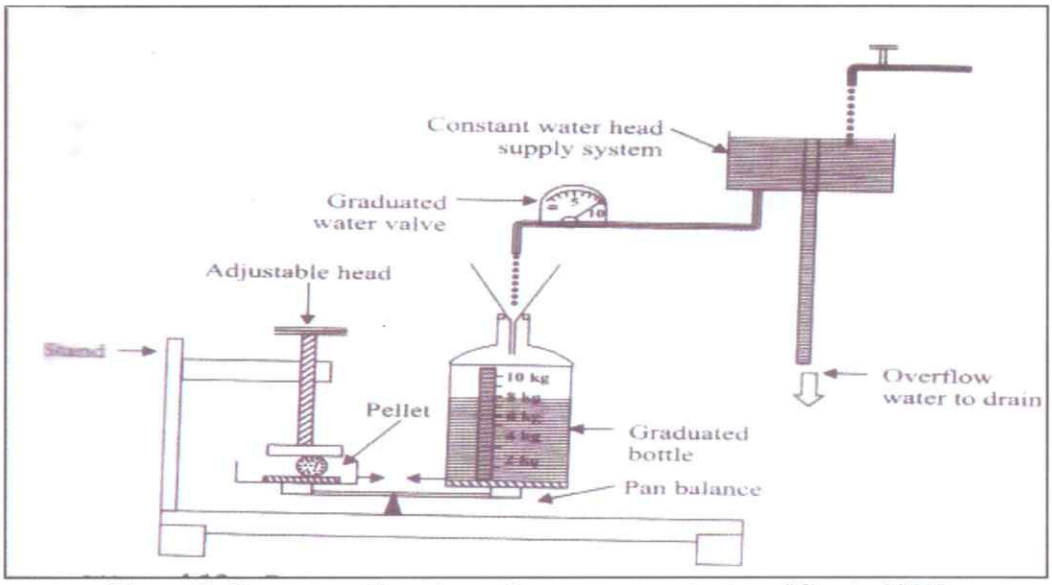


Figure 7: Green crushing strength measurement set up [Gupta,2010]

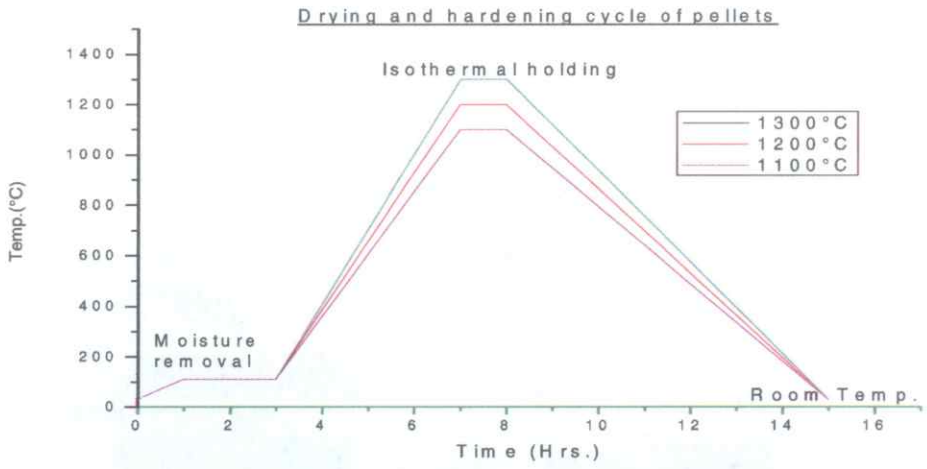


Figure 8 : Hardening cycles of Dried Pellets

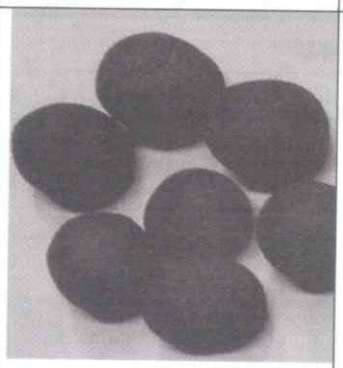
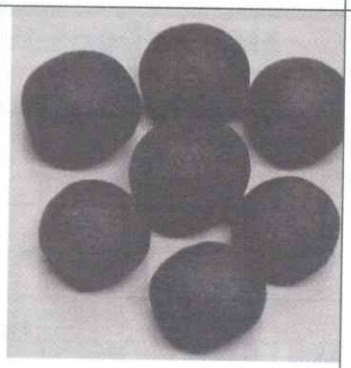
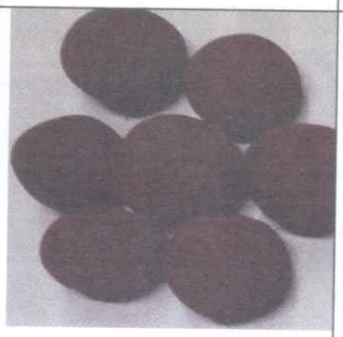
Hardening temp	Acid	Neutral	Basic
1300°C			
1200°C			
1100°C			

Figure 9: Colour changes of pellets after hardening at different temperature

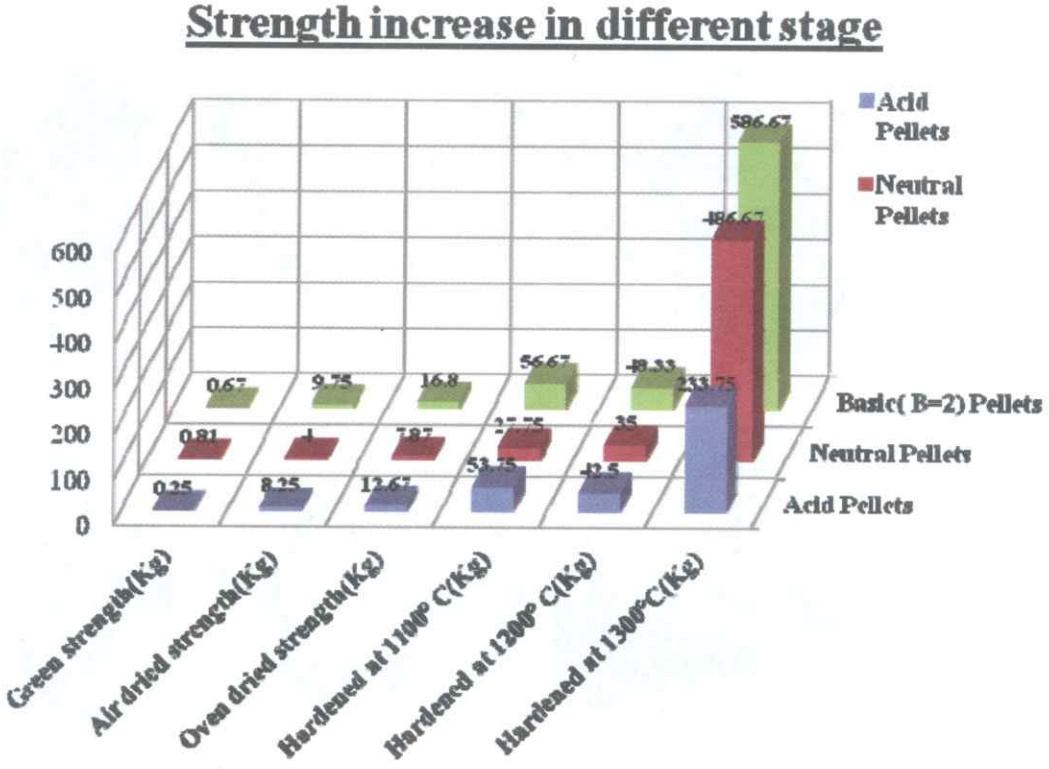


Figure 10 : Strength of the pellets varies in different stages

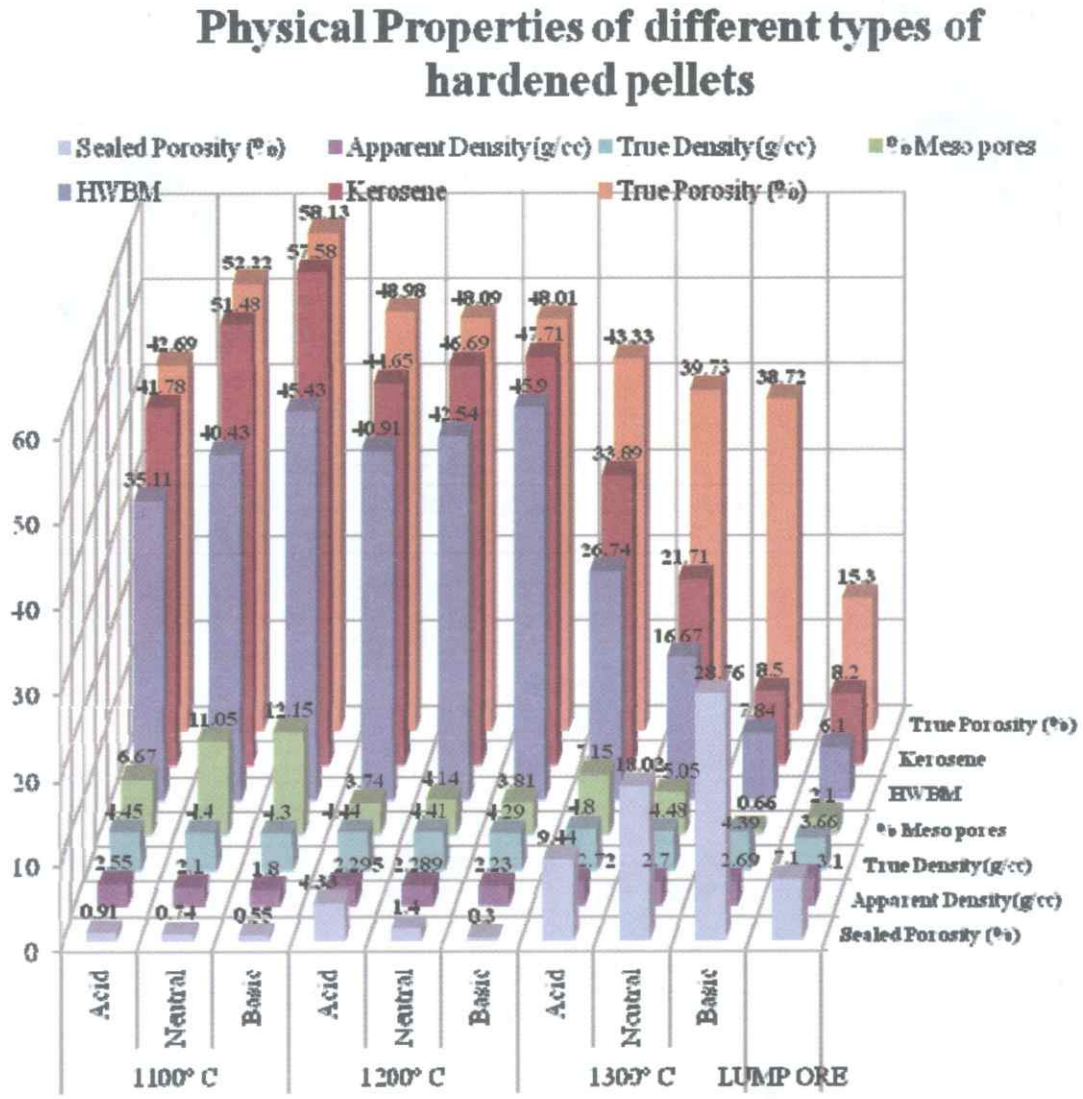


Figure 11: Physical properties of different types of hardened pellets

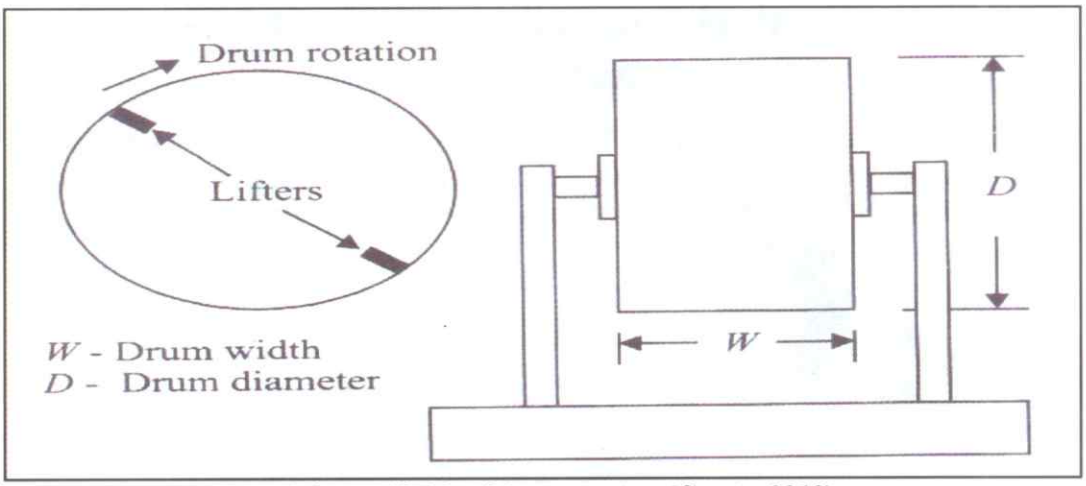


Figure 12: Tumbler test setup (Gupta, 2010)

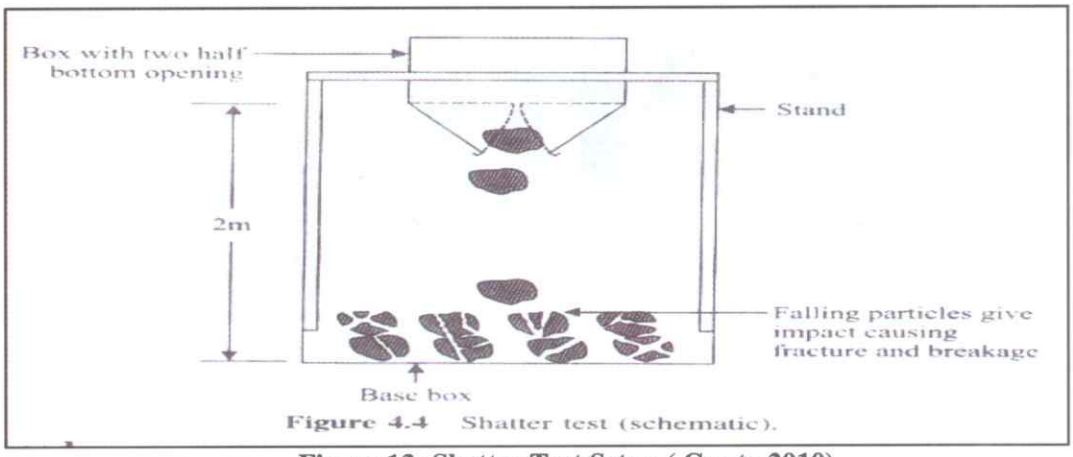


Figure 13: Shatter Test Setup (Gupta,2010)

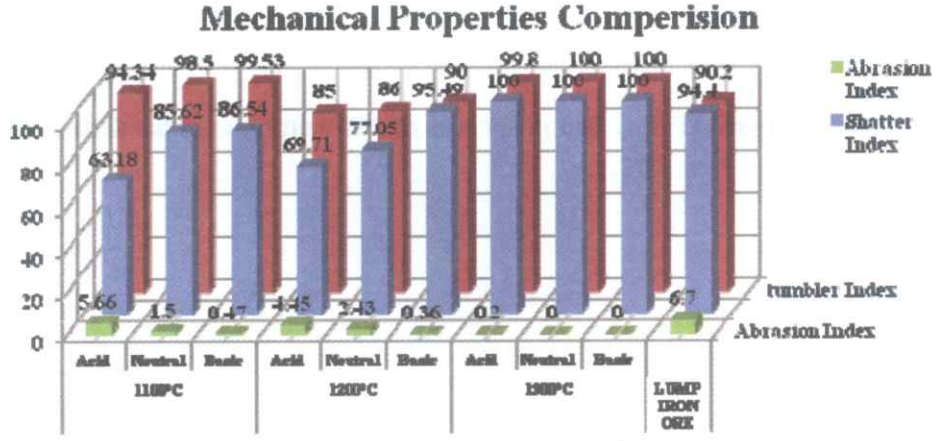


Figure 14: Mechanical properties of hardened pellets

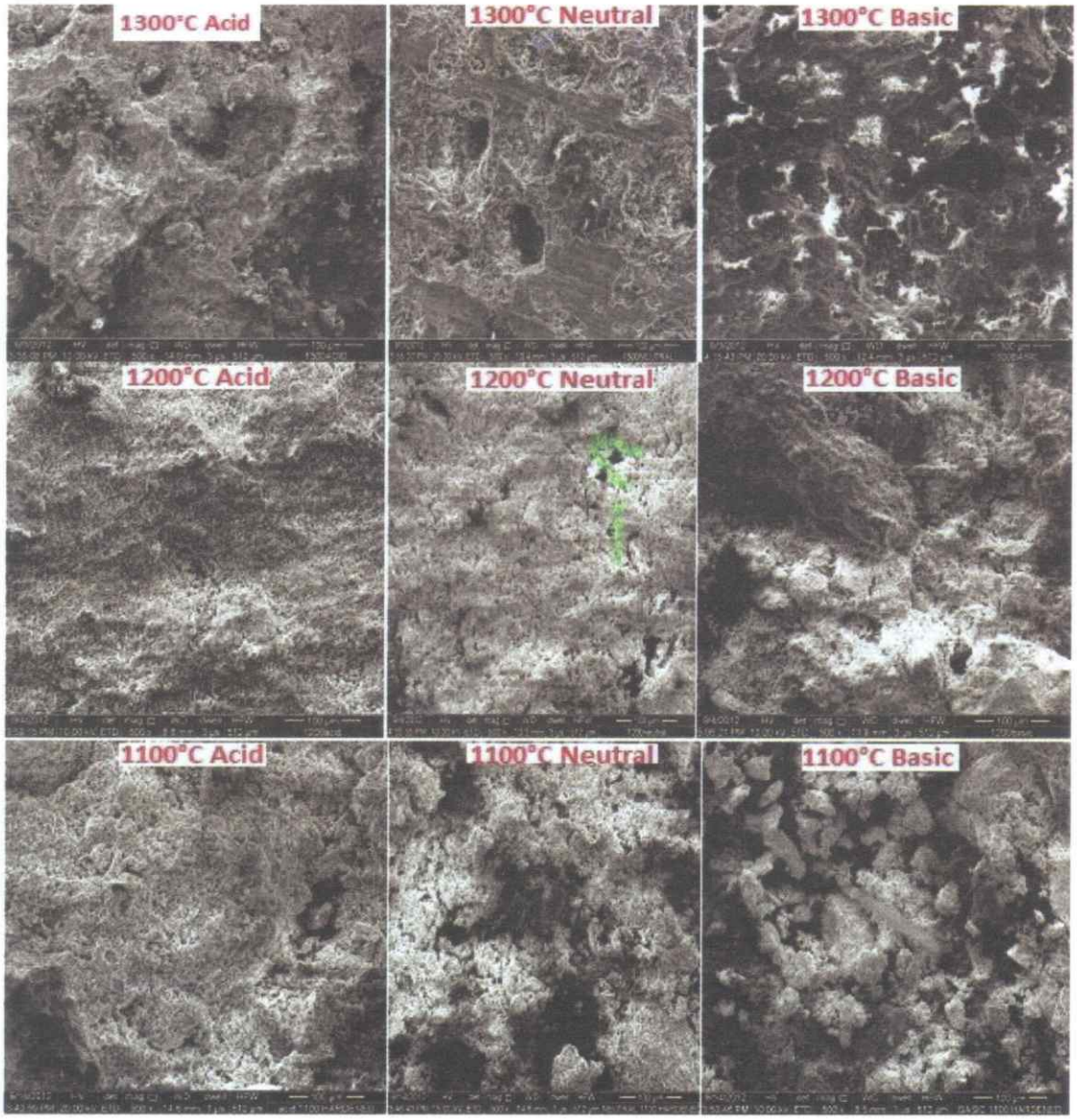


Figure 15: SEM Picture of hardened pellets

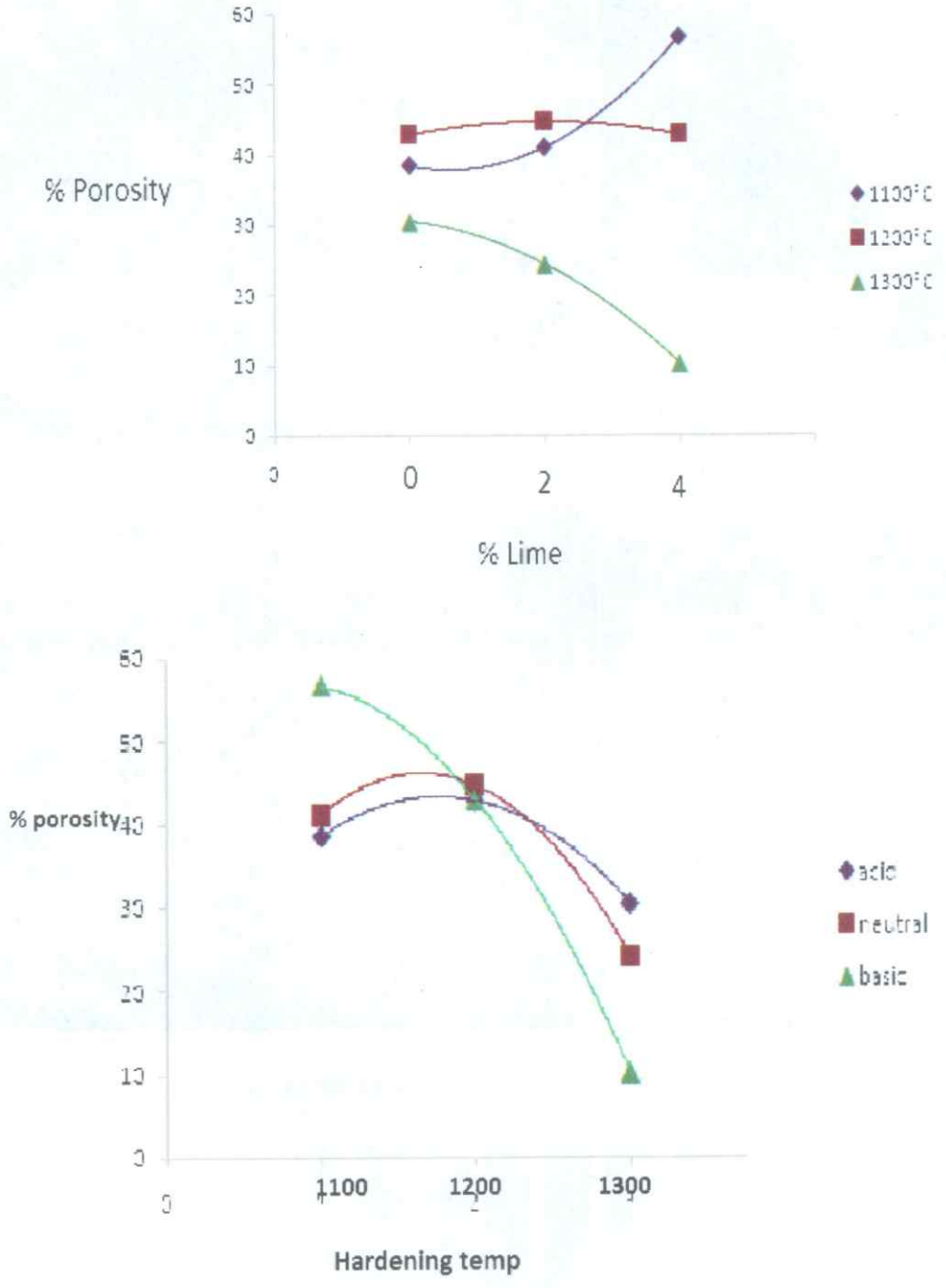


Figure 16: Effect of temperature and lime contain on porosity

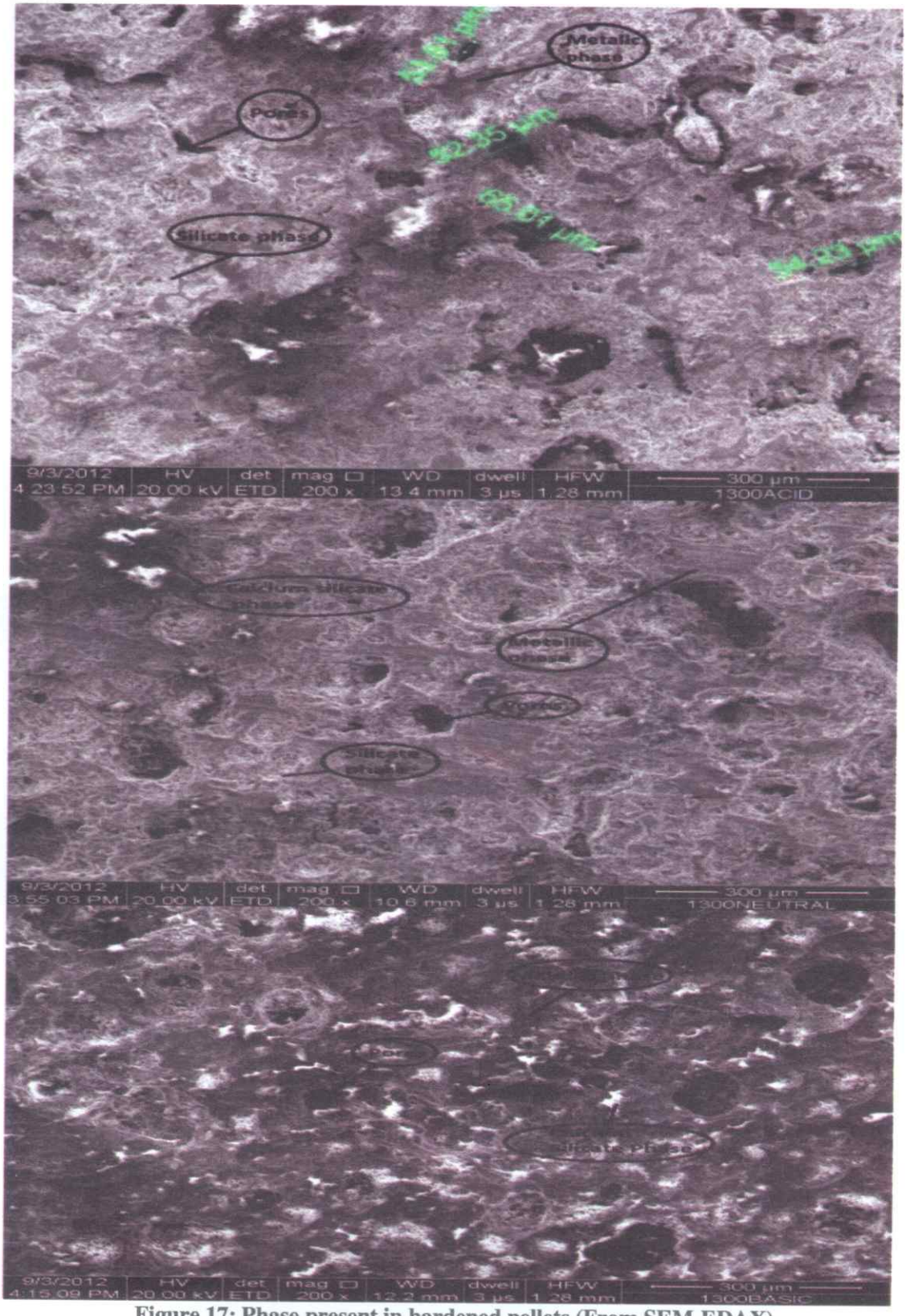


Figure 17: Phase present in hardened pellets (From SEM-EDAX)

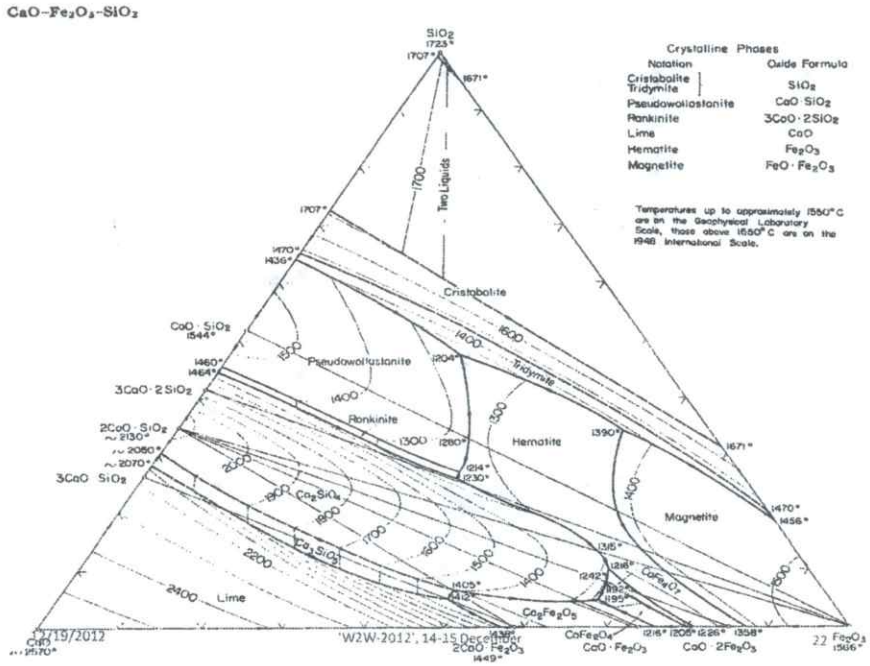


Figure No. 18: Ternary diagram of $CaO-Fe_2O_3-SiO_2$ (Source: Ernest M. Levin et al, 1964, Phase Diagrams for Ceramists, The American Ceramic Society, INC, p-228)

8. List of Tables

Table 1: Chemical analysis of Iron ore and Lime Stone

Raw Material	Fe(T)	SiO_2	Al_2O_3	CaO	MgO	Mn	P	S	Fe_2O_3	Alkali	LOI
Iron Ore fines	64	1.8	2.6	-	0.08	0.07	0.03	.001	-	0.1	2.5
Lime Stone fines	-	1.2	1	52	2	-	0.022		0.5	0.23	40

Table 2 : Composition of green pellets

Type of the pellet	Moisture(%)	Iron ore(%)	Lime addition(%)	SiO_2 input(%)	Al_2O_3 input(%)	CaO input(%)	Basicity (B_1)
Acidic	12	100	0	1.8	2.6	0	≈0
Neutral	13.5	98	2	1.784	2.62	1.78	≈1
Basic	15	94	4	1.74	2.64	3.56	≈2

Table 3: Crushing and drop strength of green Ball

Pellet Category	Size (mm)	Moisture (%)	Basicity (B_1)	Drop Strength (Nos)	Crushing strength (Kg)
Acid	15-20	12	0	3	0.25
Neutral	15-20	13	1	5	0.81
Basic	15-20	14.5	2	4	0.67

Table 4: Comparison of strength developed during drying and hardening

Nature of pellets	Basicity	Green strength (Kg)	Air dried strength (Kg)	Oven dried strength(Kg)	Hardened at 1100° C(Kg)	Hardened at 1200° C(Kg)	Hardened at 300°C (Kg)
Acid	0	.25	8.25	12.67	53.75	42.50	233.75
Neutral	1	.81	4	7.87	27.75	35	486.67
Basic	2	.67	9.75	16.8	56.67	48.33	586.67

Table 5 : Physical properties of different types of hardened pellets

Hardening temp	1100° C			1200° C			1300° C			LUMP ORE
Pellets type	Acid	Neutral	Basic	Acid	Neutral	Basic	Acid	Neutral	Basic	
HWBM	35.11	40.43	45.43	40.91	42.54	45.9	26.74	16.67	7.84	6.1
Kerosene	41.78	51.48	57.58	44.65	46.69	47.71	33.89	21.71	8.5	8.1
% Meso pores	6.67	11.05	12.15	3.74	4.14	3.81	7.15	5.05	0.66	2.1
Apparent Density(g/cc)	2.55	2.10	1.80	2.295	2.289	2.230	2.72	2.7	2.69	3.1
True Density(g/cc)	4.45	4.40	4.30	4.44	4.41	4.29	4.8	4.48	4.39	3.66
True Porosity (%)	42.69	52.22	58.13	48.98	48.09	48.01	43.33	39.73	38.72	15.3
Sealed Porosity (%)	0.91	0.74	0.55	4.33	1.4	0.3	9.44	18.02	28.76	7.2

Table 6 : Mechanical properties of hardened pellets (**non standard weight basis**)

Hardening temp	Pellets	Shatter index (%)	Tumbler index (%)	Abrasion index (%)
1100°C	Acid	63.18	94.34	5.66
	Neutral	85.62	98.5	1.5
	Basic	86.54	99.53	.47
1200°C	Acid	69.71	85	4.45
	Neutral	77.05	86	2.43
	Basic	95.49	90	.36
1300°C	Acid	100	99.8	.2
	Neutral	100	100	0
	Basic	100	100	0
LUMP IRON ORE		**94.4**	**90.2**	**6.7**

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RECOVERY OF IRON VALUES FROM BHQ ORE BENEFICIATION PLANT REJECTS

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ABSTRACT

BHQ ore fines (below 4mm size) generated as rejects by a dry beneficiation plant of Rajasthan, India were used for the present study. In this plant dry beneficiation is being practiced by simple crushing followed by dry classification. Attempts were made to beneficiate these rejects (below 4mm size) to recover the additional iron values. The rejects contains around 25.02%Fe, 61.53%SiO_2, 0.65%Al_2O_3 and 0.68% LOI. Mineralogical study indicates that hematite and quartz are the major minerals. Hematite is mostly of specularite with acicular habit. Characterisation studies revealed that the liberation size of the particles is in the range of below 150 micron. Beneficiation techniques such as WHIMS and Tabling were adopted and experiments were conducted accordingly. It is possible to increase the iron content from a feed assay value of 25.02% iron to as high as 65% iron with a yield of 34%.

Keyword: BHQ Rejects, WHIMS, Recovery, Mineralogy, Rajasthan.

INTRODUCTION

India is one of the leading producers of iron ores in the world and it can meet the growing demand of iron and steel industry in the country and also sustain considerable foreign trade. The consumption of iron ore has increased rapidly over the past decade due to the tremendous growth of iron and steel industry. As per National Steel Policy, in order to support steel production of 110 million tonnes by 2020, the requirement of iron ore is placed at 190 million tonnes per year (IBM, 2006). India is endowed with large reserves of high grade hematitic iron ores which are depleting day by day. Considering the resource position and increase in demand of good grade ore in steel production, there is a great stress on utilisation of low grade iron ores, fines, rejects as well as BHQ and BHJ ores. Exploitation of high grade iron ores has resulted in accumulation of huge quantity of low and off grade ores (often consider as rejects) over the years which are causing environment problem. It is therefore imperative to find ways and means to recover iron values from these rejects and thereby conserving natural resource and reduce the pollution hazard. Disposal of rejects generated from the iron ore beneficiation plant also causes major environmental problem, which is becoming more serious with increasing extraction of lower grade ores. Therefore, comprehensive utilization of waste/tailings/rejects is important in conserving non-renewable fast depleting natural resources and, improving surroundings for sustainable development.

In this work, an effort has been made to characterize and beneficiate BHQ ore plant rejects and prepare quality products for iron and steel industry. The present paper deals with detail characterisation and beneficiation studies of low grade BHQ ore plant rejects with an object to produce a high grade concentrate (≈ 65% Fe) in an economically viable technological process.

MATERIALS AND METHODS

Materials

The BHQ reject (below 4 mm size) generated by a dry beneficiation plant of Rajasthan, India were collected and used for this study. The as received sample of about 100 kg was thoroughly mixed and representative sample was prepared for different characterisation and beneficiation tests. Representative samples from 'as received' rejects as well as 'as received' rejects ground to below 150μ and 100μ size were taken for wet size analysis.

A representative sample was drawn from below 150μ &100μ size as feed material for beneficiation experiments.

Methods

Chemical analysis of the as received reject sample was carried out.Wet size analysis of 'as received' reject sample and 'as received' reject sample ground to below 150 μ and 100 μ size were carried out by using the standard BSS (British standard system) sieves. Each size fraction was dried, weighed and analysed for iron values.

The mineralogical characterisation of the BHQ reject sample was carried out by optical Microscope and, X-ray diffraction. .For microscopic study, a good polish section was prepared by mounting the sample in araldite and then polishing by different abrasives (carborundum powder, alumina powder).

Low grade iron ores with siliceous impurities has been upgraded by many techniques especially gravity and magnetic based processes (Burt, 1994; Svoboda, 1987). Based on the difference in specific gravity, gravity separation, such as WILFLEY shaking table was used to separate hematite from quartz. Similarly based on magnetic properties of hematite and gangue, magnetic separation by wet high intensity magnetic separation (WHIMS) units was adopted (Anupam et al., 2010).

In WHIMS, experiments were carried out by varying feed size feed size (-150μ,-100μ) and, magnetic intensity (4900, 7700, 11800, 13720, 15400 gauss). About 500 gm of sample was taken for each experiment. A slurry was prepared by adding water to a fixed amount of sample and the slurry is poured into the funnel. As the slurry is passed through an applied magnetic field (the strength of magnetic field can be changed depending on the characteristic of the sample), the sample is separated into magnetic and nonmagnetic fractions. After the experiment is over, magnetic and nonmagnetic fractions are collected, dried, weighed and analysed for iron values.

In Wilfley shaking table experiment about 3 kg of sample was taken. Experiments were carried out by varying feed size (-150μ,-100μ) and spray water flow rate (2, 4, 6 l/m). The Wilfley shaking table is used to separate large bulk sample. A slurry of sample and water moves across the table and is caught behind the longitudinal riffles. The longitudinal shaking action of the table deck causes the grains to be arranged according to their density.

When the deck is accelerated in the forward direction, the minerals will move ahead during the forward stroke.

At the end of the stroke, the direction of the motion of the table is reversed.

Due to the large inertia, heavy minerals tend to move more effectively to the end of the table, while the light minerals tend to follow more effectively the direction of the backward stroke. The water flow forces the light minerals to move slowly across the riffles down the slope of the table.

RESULTS AND DISCUSSIONS

Chemical analysis

Chemical analysis of the as received sample was given in table 1.

Table 1. Chemical analysis of as received sample.

Constituents	wt,%
Fe	25.02
SiO_2	61.53
Al_2O_3	0.65
LOI	0.68

It is evident from the chemical analysis that the sample has low iron and high silica contents.

Size and chemical analysis.

The complete size and chemical analysis of as received' sample and 'as received' sample ground to below 150 μ and 100 μ size were carried out to find out the distribution of iron in different size fraction (Figs. 1-3)

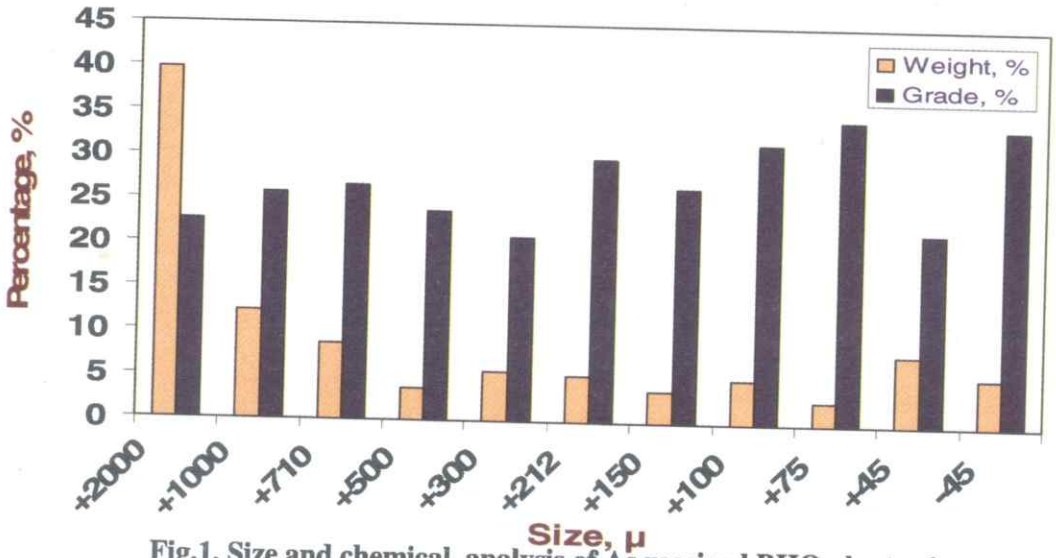

Fig.1. Size and chemical analysis of As received BHQ plant rejects

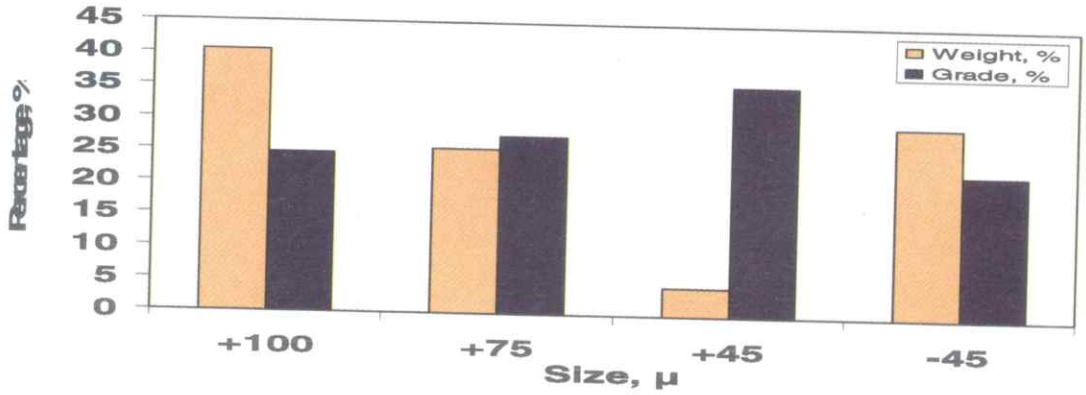

Fig. 2. Size and chemical analysis of As received sample ground to -150 μ

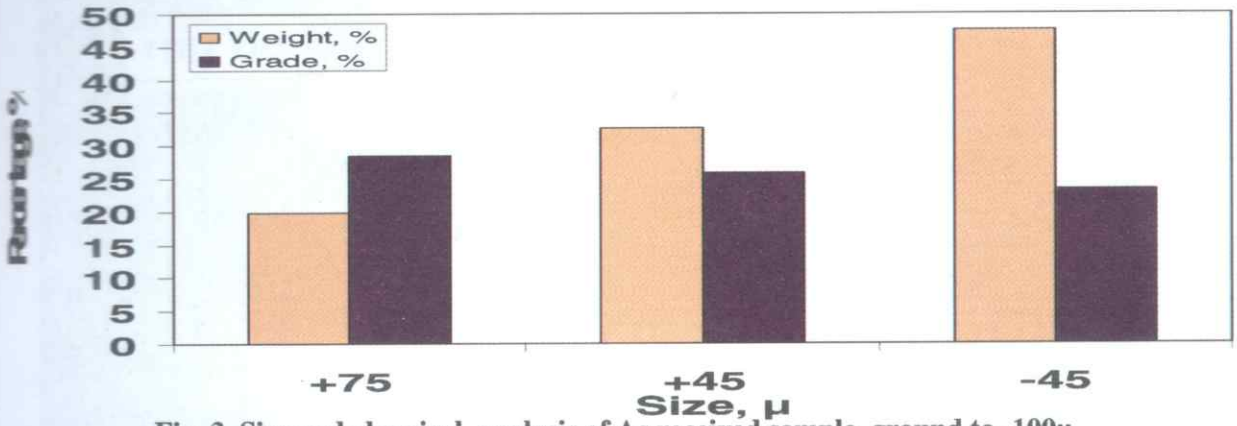

Fig. 3. Size and chemical analysis of As received sample ground to -100μ

The results indicate that in the feed sample, the iron is not uniformly distributed. in the different size fractions(fig. 1). However, by grinding to below 150μ (Fig. 2) and 100μ (Fig. 3) the iron distribution is more or less uniform.

Characterisation study:

Microscopic study:

Microscopic study revealed that hematite is the major iron mineral phase while quartz is the major gangue. As the sample belongs to Aravalli system, the BHQ has experienced some degree of metamorphism resulting in development of deformation related structures. Hematite is present as acicular grains as well as subhedral grains simulating a mosaic texture and granoblastic structure. This structure may be due to recrystallization during prograde metamorphism (Fig 4). Hematite grains show deformation twin lamellae There was lateral shifting of the twin lamellae. Euhedral to subhedral hematite grains are present within the major gangue mineral quartz (Fig. 5).The isolated and euhedral grains show effects of metamorphic recrystallization. Hematite is altered to goethite (Fig. 6). Goethite shows corrugated margin.

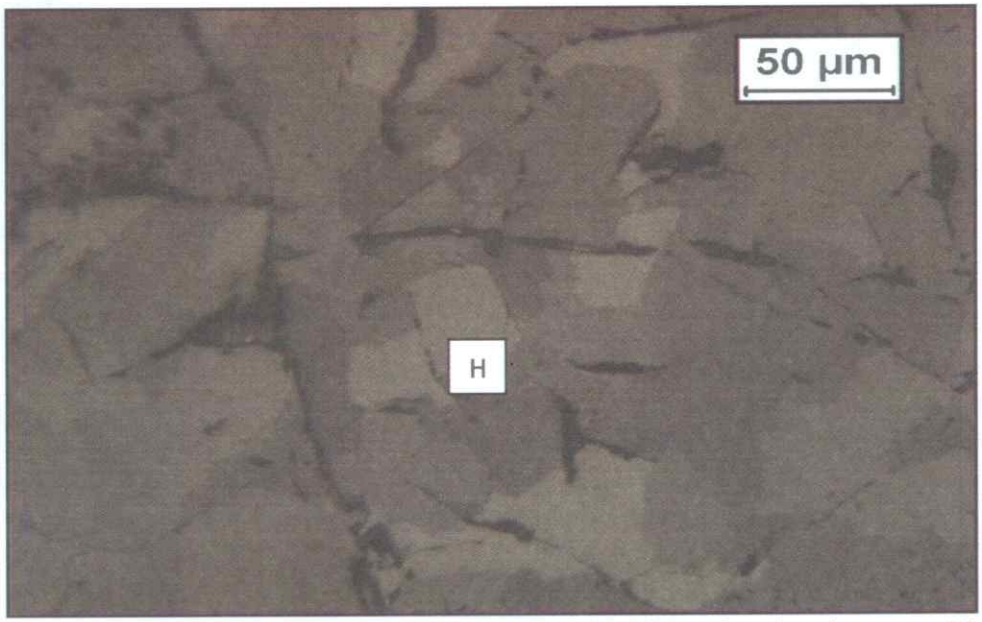

Fig. 4. Mosaic of hematite grain (H) of variable optic orientation showing granoblastic structure due to recrystallization

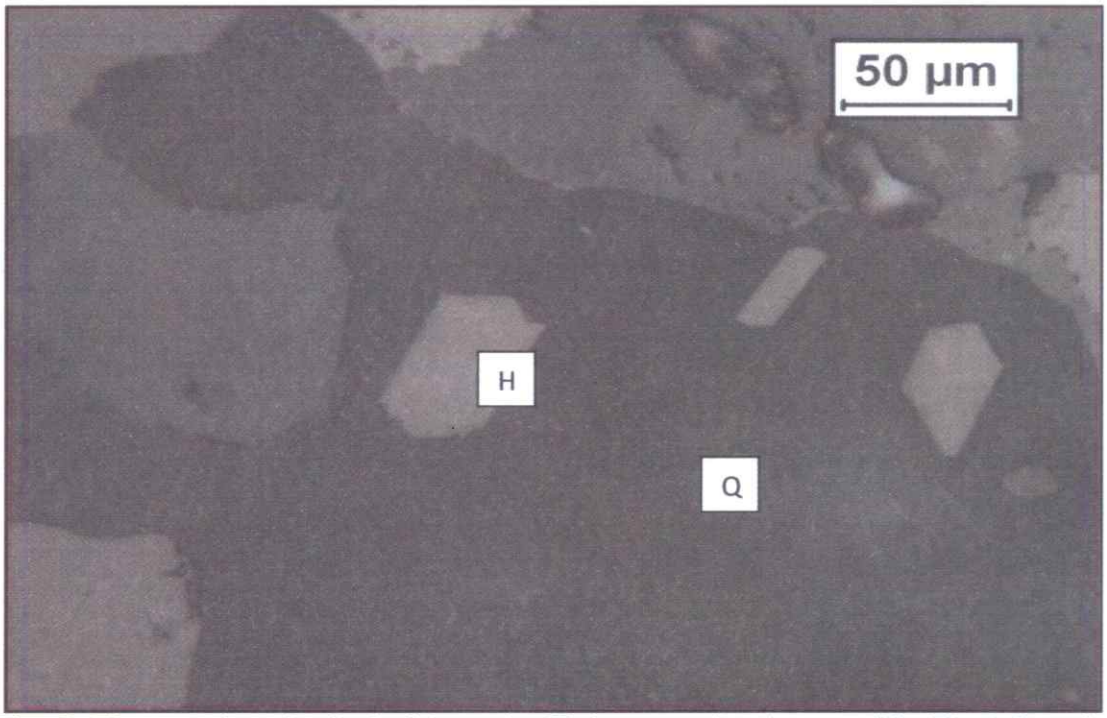

Fig. 5 Three grains of euhedral hematite(H) in a matrix of quartz(Q), The left grain shows twinning with visible re entrant. Middle grain is an elongated subhedral and to the right is seen a partial rhombohedron.- all developed by metamorphic recrystallisation.

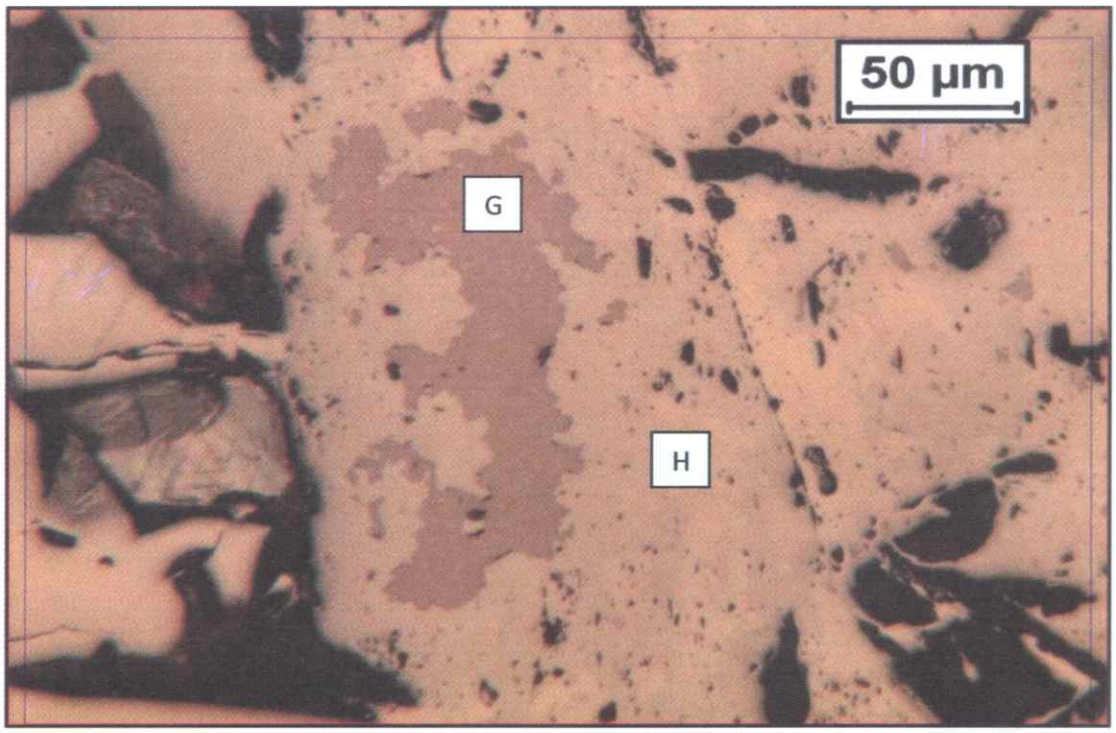

Fig.6. Goethite (G) having corrugated margin forms an island floating amidst specular hematite(H)

XRD study

X-ray diffraction technique is used to identify the minerals present in the sample.

X'pert PAN Analytical unit was used to take the X ray diffraction pattern. The pattern was obtained under the following operating conditions: Scan Axis- Gonio, Target-Cu, Kα- 1.54060 Start Position [°2Th.]-10.0100, End Position [°2Th.]-79.9900,

The diffractogram is shown in following figure 7:

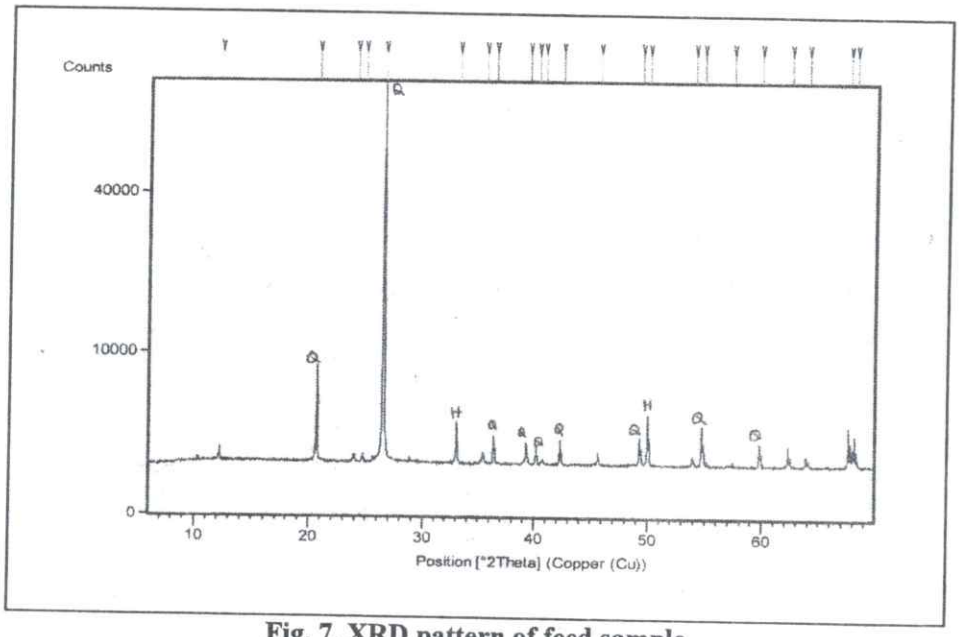

Fig. 7. XRD pattern of feed sample

From the XRD study it is concluded that the hematite is the major iron bearing mineral phase and quartz is the major gangue phase

BENEFICIATION STUDIES

Considering the mineralogical ,and chemical characteristics of the sample, beneficiation studies were carried out for enriching iron content. The salient results are discussed below.

1. Gravity separation (Wilfley shaking table)

Gravity separation was carried out by Wilfley shaking table. Experiments were conducted for both size (-150 μ and -100 μ) feed materials at different spray water flow rates. Typical results showing the effects of spray water flow rate on recovery of iron is given in the following figures:

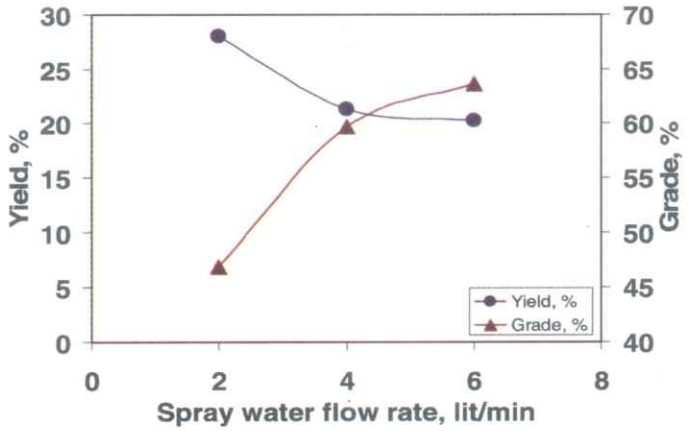

Fig. 8. Effect of spray water flow rate on grade and yield for feed material of -150 µm

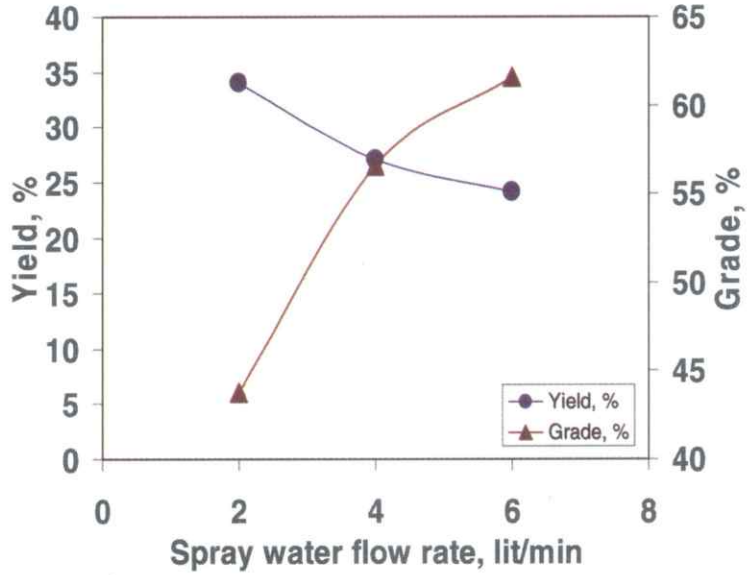

Fig. 9. Effect of spray water flow rate on grade and yield for feed material of -100 µm

Table. 2 . Effect of variation of spray water flow rate

A. Feed size: -150µm

Spray water flow rate lit/min	Yield%	Grade%
2	28.02	46.89
4	21.28	59.67
6	20.26	63.60

B. Feed size (-100µ)

Spray water flow rate lit/min	Yield%	Grade%
2	34.03	43.73
4	26.98	56.53
6	24.08	61.60

From the above figures (Fig. 11-12) and table 2, It has been observed that the grade increases with increase in spray water flow rate, simultaneously the yield decreases. It has been observed that at 6 l/m spray water flow rate with -150 micron size feed material, Fe can be up-graded up to 63.60% with an yield of 20.26% only.While using the feed material of -100 micron size, the yield increases to 26.08% with a grade of 61.60% Fe..

Magnetic separation (Wet high intensity magnetic separator)

Considering the paramagnetic nature of hematite, studies were undertaken for its recovery by wet high intensity magnetic separation (WHIMS). Attempts were made to upgrade this BHQ rejects through WHIMS for both size (-150 μ and -100 μ) feed material at different magnetic field intensities .Typical results showing the effects of magnetic field intensity on recovery of iron is given in the following figures (Fig. 13-14):

Table 3. Effect of magnetic intensity on recovery & grade

A. Feed size (-150μ)

Intensity in gauss	Yield%	Grade%
4900	22.06	66.56
7700	30.47	65.02
11800	32.54	63.23
13720	33.07	62.04
15400	33.33	60.14

B. Feed size (-100μ)

Intensity in gauss	Yield%	Grade%
4900	25.49	66.02
7700	32.29	65.05
11800	34.38	64.93
13720	34.97	61.43
15400	35.28	61.02

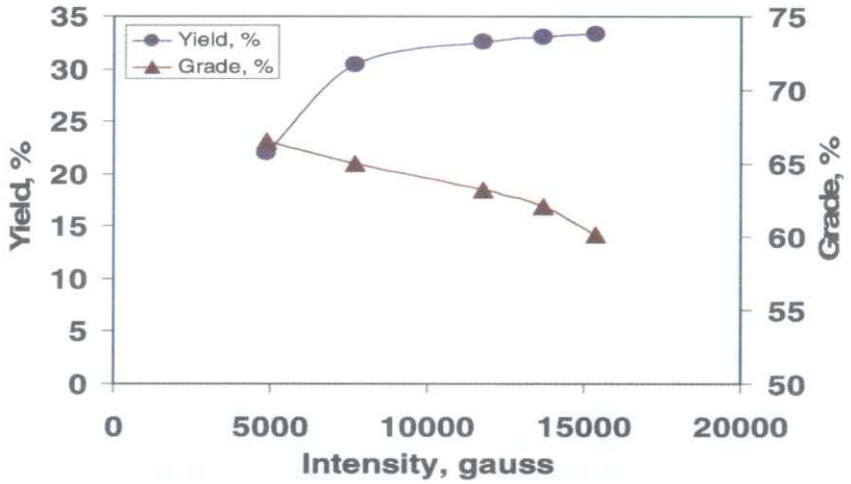

Fig.10. Effect of magnetic intensity on grade and yield of feed sample of -150μm

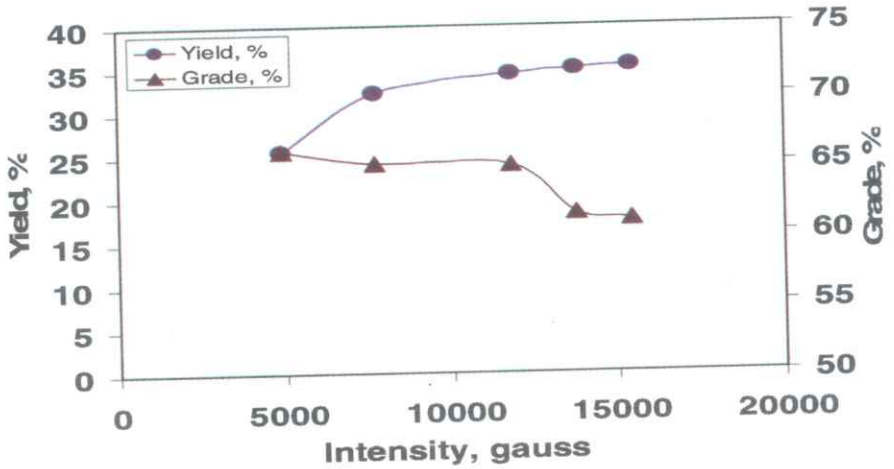

Fig.11. Effect of magnetic intensity on grade and yield of feed sample of -100µm

From the above figures and table 3. it is observed that yield increases with increase in magnetic intensity without much variation in grade.It has been observed that at 11800 gauss with -100 µ size feed material, a concentrate of 64.93% Fe could be achieved at 34.38% yield.

Below 100 micron size feed material responds well to the magnetic separation in terms of yield as well as grade of the concentrate.

CONCLUSION

The BHQ plant reject sample consists of hematite and quartz with minor amounts of goethite. Hematite exhibits various deformational textures/structures and also effects of pro-grade metamorphism. Though hematite is altered to goethite, the alteration is not pervasive one. Bulk chemical analysis indicates composition of the feed sample is around 25.02% Fe, 61.53% SiO_2, 0.65% Al_2O_3 and 0.68% LOI..Beneficiation experiment using Wilfley Table revealed that at 6 lit/min spray water flow rate with -100 micron size feed material Fe can be up-graded up to 61.60% at an yield of 26.08% only. It has been observed that by WHIMS experiment, the Fe content of the concentrate could be upgraded to 64.93% with an yield of 34.38% at 11800 gauss magnetic intensity using below 100 µ size as feed material.

From the results of two beneficiation tests carried out on this BHQ reject, it is observed that the sample responds better to magnetic separation technique compared to gravity based technique in terms yield as well as grade.

ACKNOWLEDGEMENTS

The authors express their sincere thanks to the Director, CSIR-IMMT for giving permission to publish this paper.

REFERENCES

1. *Indian Mineral year Book- (2006), pp47(Indian Bureau of Mines, Nagpur)*
2. *Burt, R.O. (1994) Gravity concentration Technology, pp. 416-431 (Elseiver-Amsterdam)*
3. *Svoboda, J. (1987). Magnetic methods for the treatment of minerals. pp. 516-527, Elseiver- Amsterdam)*

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SELECTIVE FLOCCULATION OF LOW-GRADE IRON ORE SLIMES

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ABSTRACT

In the present work an attempt has been made to study beneficiation of low-grade iron ore fines by selective flocculation. For this purpose the sample was obtained from BBH Mines, Chitradurga, Karnataka. The sample was subjected to chemical and mineralogical studies. The chemical analyses indicated 53.01% of Fe. The mineralogical analyses showed that the ore predominantly comprised of magnetite, jasper along with hematite and silicate as the gangue material. After characterization studies, representative samples were subjected for comminution to produce 80% passing 75 micron fractions. Further, the samples were subjected the settling tests in 1 l cylinder under different conditions of pH, pulp density and flocculants dosages. From the studies, it was observed that increased settling rates were obtained at pH 8-9 using different pulp densities. Apart from the above studies, test was carried out on recovery of iron using different dosage of flocculants.

INTRODUCTION

India is one of the leading producers of iron ores in the world contributing more than 7% of the production (Detailed dossier on iron ore in India, Indian Bureau of Mines, 2005) and it can meet the growing demand of iron and steel industry in the country. As per the National Steel Policy 2005, India will be producing 110 Mt/yr of steel by 2019-20. Iron ore is the principal raw material for the manufacture of iron and steel. Iron ore production has mostly been confined to the states of Jharkhand, Orissa, Karnataka, Goa and Chattisgarh. Indian iron ore is generally soft in nature with high clay content and mineralogically dominated by hematite and goethite , which typically generates more fines (~ 30 %) of total value mineral (Mandre and Panigrahi 1997) and slimes (10–25%) during mining and processing of the ore.

Utilization of fine particles of low grade nature have became important to fulfill the increasing industrial demand for steel and iron worldwide and non-availability of high grade iron ore reserves. Considering the increasing future demand of quality iron ores, limitations of the current beneficiation techniques and the conservation of iron ore resources, there is a need to develop and adopt suitable technology for beneficiation of low-grade iron ore fines. The slimes apart from having some amount of iron values and high impurities, contaminate land and water and poses threat to the environment. From the conservation and ecology points of view, it is necessary to recover the iron value since the considerable amounts of iron value are also lost. Treatment of these finely disseminated ores often results in the production of ultra fine particles, or slimes, which respond poorly to the conventional separation techniques and often lost in the process tailing.

From the literature, it is seen that processing of low- grade iron is difficult and poses special problem in achieving high-grade concentrate (Pradip, 1994; Singh and Mehrotra, 2007). In order to overcome these problems, many methods have been tried including flocculation and selective flocculation (Panda, et al 2010, Weissenborn et al 1994, Haselhuhn et al 2012). .It is seen that selective flocculation is efficiently used for the processing of low grade iron ores slimes in recent years. Selective flocculation process was envisaged for its up gradation, since it has been found the most promising avenue for beneficiating the finely disseminated ores worldwide.

Apart from beneficiation, selective flocculation process may also be used for concentration of solids, as in tailing disposal, removal of water from concentrate product, or recovery of process water. Therefore, In the present work an attempt has been made to study beneficiation of low-grade iron ore fines by selective flocculation using different type of flocculants such as guar gum & carboxy methyl cellulose (CMC).

EXPERIMENTAL

MATERIAL

The iron ore sample used in the study was obtained from Chitradurga mines, Karnataka. The representative sample obtained from the bulk was subjected for communition to produce 80% passing 75 micron fraction. The chemical analysis of the sample indicated 53.01% Fe.

FLOCCULANTS

Different polymers such as guar gum (non-ionic), carboxy methyl cellulose (CMC) of Saiguru food and gum industries, Mumbai, were used as the flocculants.

FLOCCULATION TESTS

The samples were initially subjected to the settling tests in 1 L graduated cylinder under different conditions of pH, pulp density and flocculants dosages. The required pH of the slurry is maintained using dilute HCL and NaOH. The slurry was stirred thoroughly by stirrer and allowed to stand undisturbed. The slurry inside the cylinder is allowed to settle for the given time and the slimes were siphoned off after noting the mud line height. The slimes and sand are collected separately, dried and subjected for chemical analysis.

RESULTS AND DISCUSSIONS

Initially, the representative sample was subjected for mineralogical studies under optical microscope. The microscopic analyses showed that the sample contains 20% hematite, 35% goethite, 20% limonite, 5% magnetite and 20% gangue. Form and habit of hematite and magnetite were found to be sub-hedral and anhedral respectively.

Some tests were carried out to know the settling rate and the effect of pulp density on settling rate. The results of the test carried out at different pulp densities maintained at the pH level of 9 are given in figure 1.

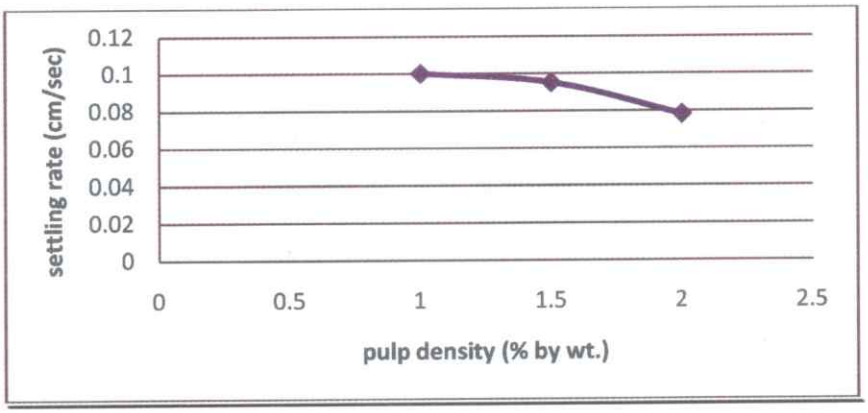

Figure 1. Settling rate as a function Pulp Density

It is seen that there is a decrease in the value of settling rate with the increase in pulp density. Maximum settling rate of the particles was

obtained at 1% pulp density by wt. Further, increase in its value leads to decreasing settling rate.

To know the effect of pH on settling rate of the particles, experimental method reported by Wills (1985) was employed. The results of the tests are given in Figure 2.

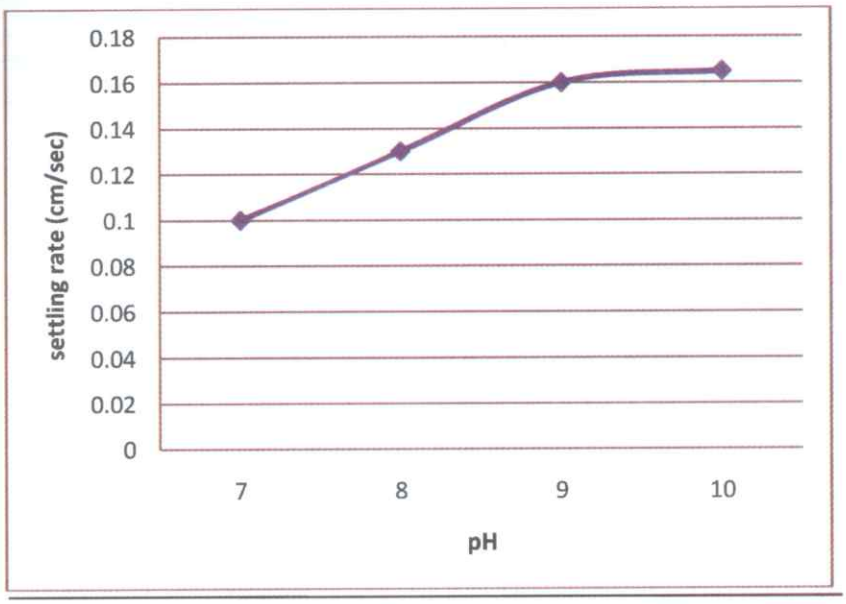

Figure 2. Settling rate as a function of pH

It is seen that settling rate of the particles increases with the increase pH value. There is marginal increase in the value of settling rate as pH value from 9 approaches to 10. This observation may be attributed to the higher quantities of fine size fractions and clayey material present, may be poorly responding to the reagent at a higher pH values.

After completion of the above tests, the sample was subjected for selective flocculation process using different flocculating agents. The pulp density of the slurry was maintained at 1% by weight at the pH level of 9. The results of the tests are given below:

Initially, the studies were carried out with the different concentrations of carboxy methyl cellulose (CMC). The results of the tests are given in Figure 3 and 4.

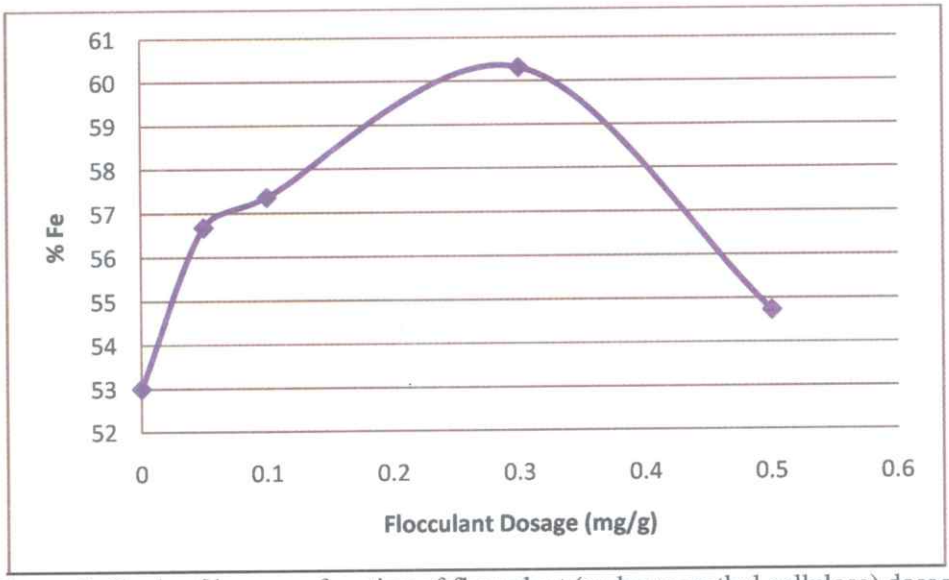

Figure 3. Grade of iron as a function of flocculant (carboxy methyl cellulose) dosage

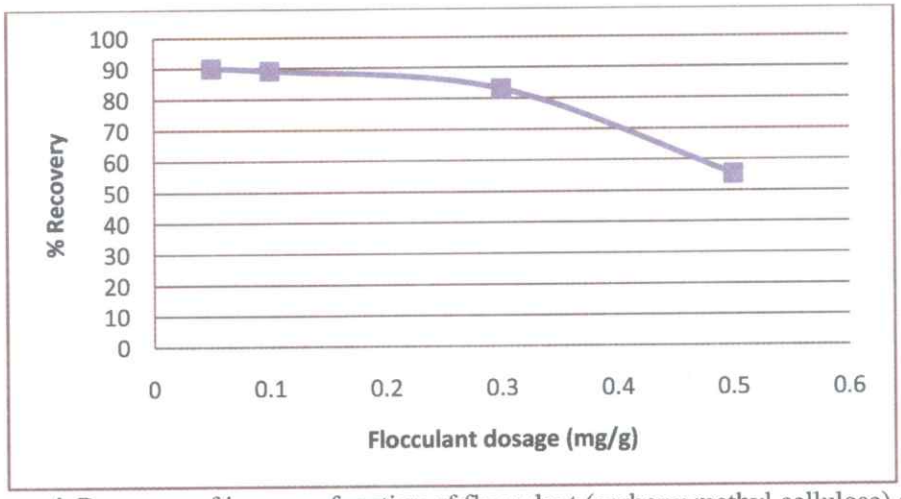

Figure 4. Recovery of iron as a function of flocculant (carboxy methyl cellulose) dosage

From these figures, it may be concluded that grade of the iron increases with the increase in concentration of carboxy methyl cellulose while the recovery of iron decreases. From the studies it was possible to achieve 60.31% iron with a recovery of 83.07% using 0.3 mg/g of flocculant. However, further increase in flocculant dosage resulted in decrease in the value of grade and recovery of iron.

Further, in order to know the effect of guar gum flocculant, some studies were carried out with different concentration of guar gum. The results of the test are given in Figure 5 and 6 for the grade and recovery respectively.

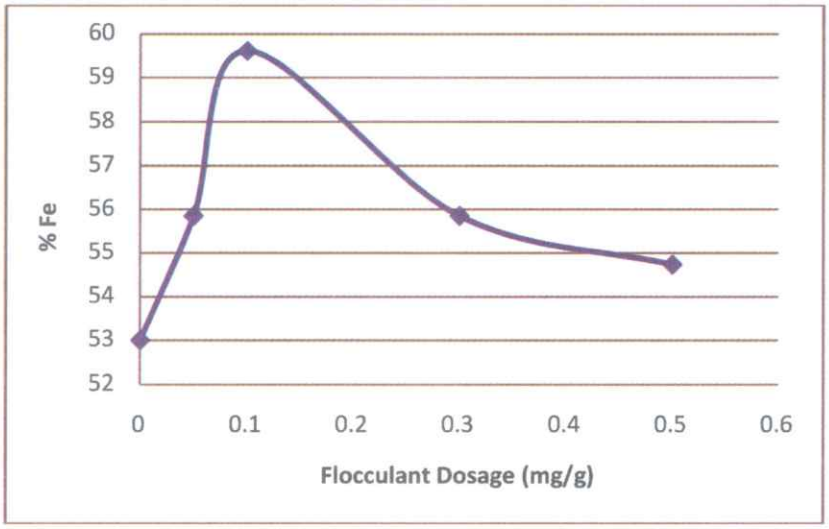

Figure 5. Grade of iron as a function of flocculant (Guar gum) dosage

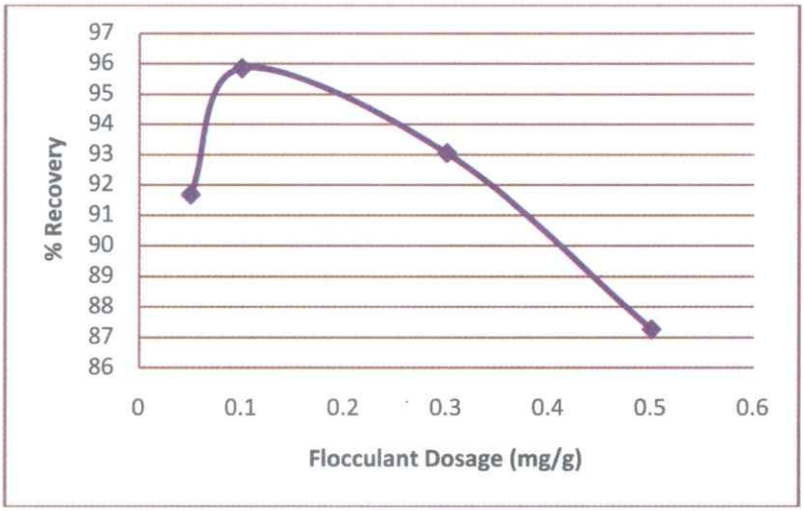

Figure 6. Recovery of iron as a function of flocculant (guar gum) dosage

When the grade and recovery were plotted as a function of floccucant, a similar pattern was obtained as in the earlier case. Maximum grade of 59.61% of iron with the recovery of 95.85% at the flocculant (Guar gum) dosage of 0.1 mg/g. Further increase in value of flocculant dosage had adverse effect on the grade as well as the recovery of the material resulted in sharp decrease in its value.

CONCLUSIONS

From the studies carried out on beneficiation of low grade iron ore, the following conclusions are drawn:

1. Iron ore samples received were pocessed of complex mineralogical nature containing 20% hematite, 35% goethite, 20% limonite, 5% magnetite and 20% gangue.

2. Selective flocculation test was carried out using different flocclulants such as carboxy methyl cellulose and guar gum. It was seen that best results were obtained using carboxy methyl cellulose (CMC) with the grade of 60.31% iron and recovery 83.07%.

ACKNOWLEDGEMENT

Authors are thankful to BBH Mines, Chitradurga, Karnataka for supplying necessary samples.

REFERENCES

Detailed information dossier on iron ore in India (2005), Indian Bureau of Mines. Chapter 1.

Haselhuhn, H J, Carlson, J J and Kawatra, S K 2012. Water chemistry analysis of an industrial selective flocculation dispersion hematite ore concentrator plant, Intl. J Miner Process, 102-103 (25):99-106.

Mandre, N R, and Panigrahi, D, 1997. Studies on selective flocculation of complex sulphides using cellulose xanthate, Intl. J Miner Process, 50:117-186.

Mathur, S, Singh, P and Moudgil, B Mafic, 2000. Advances in selective flocculation technology for solid-solid separation, Intl. J Miner Process, 58 (5-6):201-222.

Panda, L, Biswal, S K and Tathavadkar, V, 2010. Beneficiation of iron ore kaolinite mixtures using selective flocculation, Journal of Minerals and Material Characterization and Engineering, 9 (11):973-983.

Pradip, 1994. Beneficiation of alumina-rich Indian iron ore slimes. Met. Mater. Processes 6(3), 179-194.

Wills, B A, 1985. Mineral Processing Technology, pp546-549 (Pergamon Press: Oxford).

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UTILISATION OF SOLID WASTE IN STEEL INDUSTRIES

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ABSTRACT

Steel consumption is one of the important yardsticks for measurement of development and prosperity of the human civilization. Waste utilisation /recycling is very important for the sustainability of human life. Solid waste generation is indispensable for production of crude steel. The generation of solid waste is about 40% of total crude steel production. Solid waste generation is function of steel production. Thus on average 400kg of solid by product is generated in steel industry per ton of crude steel. Its major share consists of blast furnace slag and basic oxygen furnace slag. These comprise about 70-80% of total solid waste generated in steel plant. Due to continuous depletion of natural resources and regulatory norms, it has become imperative to explore the utilisation potential of these wastes. Study has been made by R&D Centre for Iron & Steel, SAIL for detailed characterisation of solid wastes and prospects of their recycling and utilisation. Research and development centre, SAIL has carried out some projects to enhance the utilisation of waste in steel plants. This paper deals about the work carried out with respect to utilisation of some of the waste generated.

Key words: Waste utilisation, BOF Slag, Blast Furnace slag, Mill scale, Mill sludge

INTRODUCTION

Generation of waste is proportional to steel production. Waste utilization is an important component of sustainability of an industry. From this perspective, steel industry has to increasingly focus on utilization of wastes. In order to render steel industry sustainable, recycling and usage of steel plant waste is of crucial importance due to increasing disposal costs, heightened environmental awareness, stringent demands by regulatory authorities for environmental protection and many of these materials are now being managed as a resource to be utilized rather than a waste to be land filled. Disposal of these wastes requires vast stretch of land. If disposed it requires detailed characterization as their dumping may affect the underground aquifers due to leaching of the heavy and toxic metals present in wastes by rain water. R & D efforts have been made for studying the utilization potential and prospects of some of the wastes - BF sludge, BOF slag, Oily mill sludge, acid sludge etc. In this paper study carried out for utilization of BF sludge and BOF slag have been described.

Part of the BOF slag generated is either recycled or reused and rest portion is dumped because of its high phosphorus and free lime content. Hence, utilization outside the steel plant is needed to be increased. The project was taken up for identifying external application of BOF slag.

Significant quantities of sludge and slag are generated as waste material or by product every day from steel industries. They usually contain considerable quantities of valuable metals and materials. It is generally possible to recover some values by physical or chemical mineral processing techniques such as crushing, grinding, classification, hydrocyclone, magnetic separation, flotation, leaching or roasting. Transforming these solid wastes from one form to another to be reused either by the same production unit or by different industrial installation are very much essential not only for conserving metals and mineral resources but also for protecting the environment[1].

In BSP's plate mill, large sized mill scale generated from the primary settling tank is fully recycled to the sinter plant. However, secondary sludge collected from the secondary settling tank consists of mill scale, oil and water, and is consequently not recycled. A major stumbling block in using the secondary sludge is its sticky

nature. The conventional methods of removing the oil would be cost - ineffective. Therefore, an unconventional method has been tried[2]. Since it is difficult to remove oil from an in-situ air dried sludge, fresh secondary sludge was slurried and decanted to separate the emulsion to partially remove oil. The decanted material was first air-dried and heated at 200 C.

Steelmaking slag has been used commercially since at least the mid-19th century.BOF slag has been safely and successfully used as a construction aggregate in many applications such as asphaltic concrete, Portland cement concrete, roadway embankment and shoulders and on unpaved roads, parking lots, walkways and driveways. Non-construction related applications include the Portland cement production, agricultural applications such as soil re-mineralization, pH supplement/liming agent, for treating acidic run-off from abandoned coal mines and for remediation of industrial waste water run-off [3].

MATERIALS AND METHODS

Blast Furnace Sludge

Pot Sintering Studies

Laboratory Pot Sintering studies were carried out considering the actual plant condition parameters. The sinter pot dia is 310 mm and bed height 400 mm, ignition time of 2.5 minutes. The lab experiments were carried out to know the effect of addition of BF sludge on sintering process parameters. The BF sludge was used in 5 kg and 10 kg/T of sinter. Charge calculation was done using mathematical model for chemistry of sinter which is produced in one of the SAIL Steel Plant.

Feasibility study on improving utilization of BOF slag

Three applications identified are

- **Use as cement substitute for making Concrete Blocks and Floor Tiles**

Concrete Blocks

Ground BOF slag was used to replace cement in various percentages like 10%, 15%, 20%, 25% and 30%. Concrete blocks **(Fig 1)** were made on a vibrating bed to make them compact. After drying, specimens were water-cured for 28 days. Then after Cold Compressive Strength (**CCS**) of blocks were measured.

Floor Tiles

For making floor tiles, BOF slag of 200 mesh (0.053 mm) size, stone powder as fine aggregate, cement and water as per standard mix design were used. BOF slag powder was used to replace cement in various percentages like 10%, 15%, 20%, 25% and 30%. All ingredients were mixed and Floor tiles **(Fig 2)** were made by Tile Making machine. After sun drying, tiles were water-cured for 28 days. Cold Compressive Strength (**CCS**) of Floor Tiles was measured.

Fig 1: Concrete Blocks

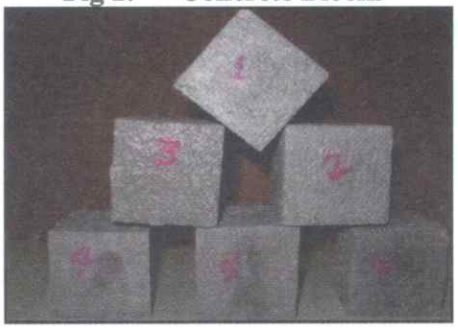

Fig 2: Floor tiles

2. Use as neutralizing & conditioning agent

Water samples of coal mines of Jharkhand area are not of acidic nature, therefore, water samples were made acidic (pH of coal mines runoff water are generally 2.5-4.0) to check the neutralizing potential of BOF slag. Acidic water samples were then treated with BOF slag in various proportions and its feasibility in the laboratory was established. 1.0 gm of BOF slag was found effective for neutralizing 100 ml mines water of acidic nature. Results of using BOF slag as neutralising and conditioning agent are shown in Table 4.

3. Up-gradation of BOF slag properties for transport sector applications

Natural ageing is a slow process and to accelerate the process high pressure steam is used. For steam ageing of BOF slag, an apparatus made of stainless steel was conceptualized, designed and fabricated to withstand a pressure of 6 kg/cm^2. Ageing experiments of slag were conducted by varying the different parameters like time, temperature and size fractions. Alkalinity, pH and percentage of CaO were taken as marker parameters for completion of hydration.

RESULTS AND DISCUSSION

Chemical composition of a typical sludge from Blast Furnace is given in Table 1.

Table 1: Chemical composition (Wt %) of a typical sample of BF Sludge

Fe(T)	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	S	Carbon content
33.43	8.80	5.18	5.56	1.17	-	1.50	0.20	0.61	21.27

Fe content and carbon content make the BF sludge to be utilised. Lab scale pot sintering experiments reveal that use of 10 kg BF sludge per Ton of sinter has no detrimental effect on quality of sinter.

Chemical composition of a typical sample of BOF slag is given in Table 2.

Table 2: Chemical composition (Wt %) of a typical sample of BOF slag

Fe(T)	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	S	MnO
17.06	9.75	0.77	54.27	2.81	0.17	-	0.43	0.07	1.51

Cold Compressive Strength (**CCS**) of blocks and Floor Tiles were measured. Test results have been shown in Table 3.

Table 3: Cold Compressive Strength (CCS) of Concrete Blocks & Floor Tiles

Sl No.	Use of BOF slag	Concrete Blocks	Floor Tiles
		CCS Kgf/cm^2	CCS Kgf/cm^2
1	Without replacement	**380**	**420**
2	10 %	**344**	**378**
3	15%	**212**	**354**
4	20%	**208**	**344**
5	25%	**208**	**312**
6	30%	**172**	**284**

10% to 30% of cement can be replaced by BOF slag for making floor tile, concrete blocks etc. The percentage may vary as per the chemical composition of slag used.

2. Use as neutralizing & conditioning agent

BOF slag can be used successfully to treat mines runoff water and other effluents of acidic nature. It can also be used as mine stowing material without impacting environment.

3. Up-gradation of BOF slag properties for transport sector application

BOF slag can be used for road making and as rail ballast after its ageing. Natural ageing takes more than one year where as ageing by saturated & pressurized steam takes only two hours.

CONCLUSIONS

Wastes generated in integrated steel plants require detailed physical and chemical characterization for evolving utilization prospects. Blast furnace sludge up to certain level can be utilized in sinter making without affecting the quality and productivity of sinter.BOF slag can be utilized as neutralizing agent, and making of blocks and tiles replacing cement to some extent.

ACKNOWLEDGEMENTS

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REFERENCES

1. *B. Das, S. Prakash, P.S.R. Reddy, V.N. Misra, "An overview of utilization of slag and sludge from steel industries" Resources, conservation and recycling, Vol 50, No. 1, pp 40-57, 2007.*
2. *S. Mitra Mazumder, V. R., Deshmukh, G. D. Maheshwari, S. Bhattacharya, S. N. Tiwari, S. Prakash, & H. R. Murty, "Recycling potential of secondary mill sludge", Steel Times International, 2006, 30(7), 22.*
3. *Rustu S. Kalyoncu,"Slag,- Iron & Steel", 2000,71.1.*

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RECOVERY OF STRUVITE FROM AMMONIACAL WASTEWATER BY CHEMICAL PRECIPITATION – A NEW APPROACH IN OPTIMIZATION AND DOWNSTREAM PURIFICATION

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ABSTRACT

Ammonia present in high concentration in industrial wastewater like coke wastewater can be recovered as a valuable by-product known as struvite quite economically provided the process is well optimized and an efficient downstream purification approach is adopted. This paper discusses how such process optimization and efficient downstream purification can be achieved. A central composite design of response surface methodology (RSM) was employed to investigate the effects of concentrations of phosphate, magnesium and pH value on nitrogen recovery (95%) in the form of struvite (9.5 g/L). RSM was applied to assist in understanding the relative significance of reaction factors and the interactive effects of solution conditions. The kinetics of struvite formation was systematically studied under the conditions of different molar ratios of magnesium and phosphate salt in the system. A first-order kinetic model was fitted well to the experimental results obtained. Equilibrium concentration (C_e) and the reaction rate constants (K) were determined for all cases evaluated. A membrane-integrated continuous approach was also investigated for struvite production from coke wastewater and its treatment. Two consecutive cross-flow membrane modules were fixed incorporating microfiltration and nanofiltration membranes for the separation of struvite and removal of more than 90% total suspended solids, conductivity, salinity and alkalinity, cyanide and phenol respectively. The struvite was characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR) as well as X-ray diffraction (XRD). The elemental analysis was done by using SEM electron diffraction spectroscopy (SEM-EDS). Surface characterization analysis indicated that the main component of the precipitates was magnesium ammonium phosphate ($MgNH_4PO_4$). The thermal decomposition of struvite was also studied by thermo gravimetric analysis at heating rate 10^0C per minute. Through gradual loss of ammonia and water molecules, ultimately struvite was found to be transformed into amorphous magnesium hydrogen phosphate which was confirmed by FTIR analysis after TGA.

Keywords: ***wastewater, struvite, nutrient removal, response surface methodology, membrane filtration***

INTRODUCTION

In recent years due to high demographic and industrial development that has occurred has produced an increased in water pollution. The growing demand for steel production in developed and developing countries has led to the accumulation of large volumes of coke wastewater. During the recovery of coal coking, coal gas purification and by-product recovery processes in the coke plants large amount of coking wastewater is being generated. Industrial wastewater like coking wastewater usually contains high and toxic concentrations of ammonium nitrogen, phenolic compounds, cyanide, thiocyanide and polynuclear aromatic hydrocarbons (PAHs) [Wang et al. (2008); Kumar et al. (2011)]. Due to hydrolytic and fermentative processes in biological nutrient removal (BNR) wastewater treatment plants undergo a gradual enrichment of nitrogen and phosphorus content in sludge line supernatants leads to eutrophication in fresh water bodies [Battistoni et al. (2005)]. Eutrophication problems quite common by the nutrient discharge to natural waters result in grave consequences for aquatic life as well as for water supply for industrial and domestic uses. One of the essential nutrients that can lead to water eutrophication is Ammonium nitrogen (Liikanen and Martikainen, 2003). It is not only hazardous but may

pose a threat to environment, aquatic life and human health if disposed untreated to water bodies (Han et al., 2011). Now, nutrient removal from wastewater is becoming an increasing challenge for the operators of the industries as regulatory bodies from the pollution control board tighten discharge standards to avoid eutrophication problem in receiving waters. Adequate carbon sources required for the treatment of high strength ammonia in conventional methods like biological treatment (nitrification/denitrification). This method is economical but often fails due to inhibition of microorganism growth due to high concentration of ammonia. Development of new techniques to recover nitrogen is essential in the current scenario. High strength ammonia concentration may be removed by adding magnesium and phosphate salt to form magnesium ammonium phosphate hexahydrate (MAP), a useful by-product [Stratful et al., (2001)]. MAP is commonly known as struvite, is a white crystal substance consisting of equal molar concentration of magnesium, ammonium and phosphorus. The first and the most important step is the optimization of magnesium and phosphate salt with respect to ammonia and pH value for the struvite crystallization. In the Response Surface Methodology (RSM) the mutual interactions of the parameters are smoothed out by applying Central Composite Design (CCD) approach by changing more than one process parameters at a time in optimisation experiment.

THEORETICAL BACKGROUND

The basic chemical reaction to form MAP has been expressed as Eq (1) [Doyle and Parsons, (2002)].

$$Mg^{+} + NH_4^{+} + PO_4^{3-} + 6H_2O \Leftrightarrow MgNH_4PO_4.6H_2O \downarrow; pK_s = 12.6(25^{\circ}C) \quad (1)$$

As the precipitation of the struvite reduces the pH of the solution, therefore HPO_4^{3-} will take place in the reaction rather than PO_4^{3-} as follows

$$Mg^{+} + NH_4^{+} + HPO_4^{2-} + 6H_2O \Leftrightarrow MgNH_4PO_4.6H_2O \downarrow + H^{+} \quad (2)$$

A first-order kinetic model was applied to the experimental data obtained. A slightly modified first-order kinetic model was used to calculate the kinetic constants from the experimental data obtained. The disappearance of a reactant (-dC/dt) to the rate constant (K) and the reactant concentration at time t (C) minus the reactant concentration at equilibrium (C_e) through Eq (3):

$$-dC/dt = K\ (C - C_e) \quad (3)$$

MATERIALS AND METHODS

Raw Wastewater Characterization

Raw wastewater obtained from the ammonia liquor tank of Durgapur Project Limited, West Bengal, India, a coal based power plant was analyzed and characterized in the laboratory. Table 1 shows some parameters of the wastewater sample.

Materials

In the present study all the chemical reagents were analytical grade. Chemicals like magnesium chloride, magnesium oxide, magnesium sulphate, sodium biphosphate, ortho-phosphoric acid, calcium hydrogen phosphate, hydrochloric acid, sodium hydroxide were purchased from Merck India Ltd. Standard solution of ammonia and cyanide (1000 mg/L), were purchased from Merck (Germany). Deionised water from Milli-Q purification system (Waters, MA, USA) was used for

preparing all working solutions of required concentration. Poly vinylidene fluoride (PVDF) microfiltration membranes and thin film composite polyamide nanofiltration (NF1) were procured from Membrane solution and Sepromembranes Inc. (USA) respectively.

Experimental Set-Up

The experimental set-up for struvite recovery from industrial wastewater consists of three 30 litres capacity continuous stirred tank reactors (CSTRs) for pre-treatment,crystallization reactor and struvite separation unit by flat-sheet, cross-flow mode membrane filtration module with effective filtration area100 cm^2 (Figure 1).

EXPERIMENTAL PROCEDURE

Response Surface Optimization and Continuous Mode Treatment

Effects of pH, molar ratio of Mg: NH4: $PO4^{-3}$ and concentrations of magnesium and phosphate salts on ammonia removal were studied. All batch experiments were performed in 1 L glass beakers with magnetic stirrer operating at 125 rpm to mix the sample and keep the precipitate in suspension during precipitation-crystallization process. The samples obtained during the experiment were filtered through a 0.45 µm filter to check the residual ammoniacal-nitrogen concentration. Struvite recovery for ammonia removal was optimized through laborious experimentation using response surface methodology (RSM) of Design Expert software (Design-Expert® Version 8.0.6 (serial 9l no 7020-7114) State-ease, Inc.) and the optimum concentrations for the reagents (magnesium and phosphate salt) and the optimum pH were determined. RSM utilises its statistical device that uses experimental data produced from definite experimental design to model and optimizes any process in which several variables influence the desired response (Silva, et al., 2004). By performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the responses and examining the adequacy of the model the major steps involved in optimization (Myers and Montgomery, 1995)RSM helps to compute the relationships between input variables called factors (X_is) and output variables called responses (Y) (Silva, et al., 2004). Central Composite Design (CCD) was used in this study. As it is suitable for fitting a quadratic surface, it requires minimum number of experiment to optimize the effective parameters as well as to analyse interaction among parameters (Hameed, et al., 2008). Generally, the CCD consists of a 2^k factorial runs with $2k$ axial runs and k_c central run. Each variable in CCD is investigated at two levels and as the number of variables or factors i.e. k increases, the number of runs for a complete replicate of the design increases rapidly. The central points are used to evaluate the experimental errors and reproducibility of the data. For three factors (k =3) the rotatable designs are most effective and suggested. Total number of experiments with different combinations of three variables (ratio of Mg: NH_4 (0.75-2.5) and PO_4^{-3}: NH_4 (0.5-1.5) and pH 7.0- 10.0) was 20 ($2^k + 2\,k + k_c$), where k denoted the number of variables and k_c (= 6), the number of central points for a three variables system. Required experiments were calculated from Eq. (4) as:

$$N = 2^k + 2k + n_0 = 2^3 + 2\times 3 + 6 = 20 \quad (4)$$

The coded form of five different levels for each experiment are +α, -1, 0, +1, -α. The number of factors decides the value of α in the factorial portion of the design. The value of α was fixed at 1.682 as shown in Eq (5).

$$\alpha = 2^{3/4} = 1.682 \quad (5)$$

The Eq. (6) shows the relationship between the coded and uncoded form of the variables.

$$\text{Coded value} = x_i = \frac{(X_i - \overline{X_i})}{\Delta x} \quad (6)$$

Where X_i is actual value of the ith factor in the uncoded form, $\overline{X_i}$ is the average of minimum and maximum values for the ith factor, and Δ X represents the step change. Empirical model can be built to find out the true relationship between the dependent variable and set of independent variables, i.e., the single-response modelled using the RSM correspond to independent variables. The following quadratic equation may explain the behaviour of the system.

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_{ii}^2 + \sum b_{ij} x_i x_j \quad (7)$$

where Y is the predicted response, b_0, b_i, b_{ii} and b_{ij} are the offset terms, the linear effect, the squared effect and the interaction effect respectively and x_i and x_j represent the coded independent variables.

In present work, a second order polynomial equation was obtained using the uncoded independent variables as below:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{11} X_{11}^2 + b_{22} X_{22}^2 + b_{33} X_{33}^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 \quad (8)$$

To evaluate the coefficient of the model, multiple regression analysis technique was used. Ammonia removal through struvite formation experiments were carried out batch-wise in1L glass beakers with a working volume of 500 ml in one magnetic stirrer operating at 125 rpm to mix the sample and keep the precipitate in suspension during precipitation-crystallization process at ambient temperature for duration of one hour. Investigations on ammonia removal following struvite formation by precipitation reaction were done in continuous system subsequently with the optimum doses of magnesium and phosphate compounds. The pH of the treatment medium was adjusted by addition of sulphuric acid (HCl, 2N) and sodium hydroxide (NaOH, 2M). The magnesium ammonium phosphate (MAP), slow releasing fertilizer which is popularly known as struvite resulted from the reactions of ammonia of wastewater and the added magnesium and phosphate compounds got separated in the reactor by flat-sheet PVDF microfiltration under low pressure (around 2.5 bars) in cross-flow mode. Micro filtered water was subsequently passed to a second nanofiltration membrane module where almost all the charged as well as non-charged particles got separated out from the stream following Donnan-steric mechanisms of nanofiltration [Kumar et al. (2011)]. Finally permeate, treated water was collected from the nanofiltration membrane module that was operated at around 15-16 bars pressure.

Analytical Determination

Orion 4 Star pH ISE Benchtop Ion Meter of Thermo Electron Corporation (USA) analysis for cyanide, ammonia and pH was done. The electrodes were first calibrated using the previously prepared standard of respective compounds. Chemical Oxygen Demand (COD) was measured by COD Vario Tube Test MR (0-1500mg/l) of COD analyser of LoviBond. The phenol content was determined by HPLC (Agilent Technologies 1200 series, USA) with Zorbax SB-Phenyl column (Germany) having mobile phase methanol: water (70:30) at flow rate 1mL/min, residence time of 3.5 minutes and injection volume of 5 µl.Total dissolved solids (TDS), conductivity and salinity were measured by InoLab Cond 720, with electrode

TetraCon 325 (WTW, Germany). Oil and grease were determined following the standard procedures described in the standard methods [APHA]. During nanofiltration percentage removal of pollutants were calculated using the initial concentration (C_i) of the pollutants in the feed sample and the residual concentration (C_f) in the permeate side respectively using Eq (12) as given below.

$$\% \text{ removal of pollutants} = \left(1 - \frac{c_f}{c_i}\right) \times 100 \quad (9)$$

FT-IR Analysis

Fourier transform infra-red (FT-IR) spectroscopy (Nicolet iS10, Thermo Fischer Scientific, USA) was done for MAP precipitates. The collected precipitates were washe with pure water for three times, dried in an oven at 45°C for 48 h, and then analysed by Fourier transform infra-red (FT-IR) spectroscopy. For FT-IR study, 40 mg of KBr (Merck) was mixed well with 2 mg of finely ground sample for the preparation of transparent pellets, for the determination of functional groups.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDS, S-3000, Hitachi Japan) study of MAP was done to get its crystalline structure, size of the crystal and surface composition of precipitates. SEM photograph was taken with scanning electron microscope (HITACHI – S3000 N, Japan) at the required magnification at room temperature. The working distance of 25 mm was maintained and acceleration voltage used was 15 keV, with the secondary electron image (SEI) as a detector.

X-Ray Diffraction (XRD)

The collected precipitates were washed with pure water for three times, dried in an oven at 45°C for 48 h, and then analysed by X-ray diffraction (XRD, D/max-RB, Rigaku, Japan) with a Cu-target operated at 40kv, 100mA at a scan rate of $0.1^{\circ}s^{-1}$.
Thermo Gravimetric Analysis (TGA)

TGA analysis of struvite was done (DTG-60H, Shimadzu, Japan) to get the heating profile at 10^{0}C/min under nitrogen gas environment. The conversion of the TGA curve to its derivative mode (DTGA) was undertaken from the rate of mass loss curve as a function of temperature.

RESULT AND DISCUSSION

Effect of Molar Ration on Ammonia Precipitation

$Mg:NH_3:PO_4^{-3}$molar mainly influences the MAP precipitation among other various factors in industrial wastewater. As seen in Figure 2, the variation of ammonia concentrates in the filtrate with time by using four different types of stoichiometric ratio of magnesium and phosphate salt with ammonia concentration. A rapid loss of ammonia concentration was achieved during the first 40 min, this effect being more pronounced in the case of high magnesium concentration. Moreover, the increase of the molar ratio contributed to the increase in ammonia removal and caused a decrease in equilibrium concentration (C_e), showing that the reaction was more complete. As can be seen in Figure 2 plot of $-\ln[(C-C_e)/(C_0-C_e)]$ versus time gave straight line with different slopes and intercept equal to zero in all four different combination of chemicals. As the straight lines obtained, it suggests that the first-order kinetic model proposed fixed adequately to the experimental data. The values of the linear regression coefficient were greater than 0.94 in all cases. Table 2 summarizes the values of the first-order rate constants (K), C_e and R^2 obtained from the different molar ratios.
Response Surface Optimization of Ammonia Precipitation

Experiments were planned and conducted following central composite design

(CCD), considering the minimum and maximum levels for molar ratio of $Mg:NH_4^+$ (0.75 to 2.50), $PO_4^{-3}:NH_4^+$ (0.5-1.5) and pH (7.0-10.0) and experimental results were incorporated in that design (Table 4). In the study ammonia concentration was fixed 3500 mg/L. These ranges of the variables parameters were fixed based on the data as reported in the literature in various studies of ammonia removal through struvite precipitation. In determining the interrelationships of those variables, second-order polynomial equation was fitted to the experimental data of ammonia removal (%). From fit summary section in design, the model F-values as obtained (108.58) implied that model was significant. Value of *P* (0.0001) in this case being less than 0.05 also indicates that the model term is significant. The final regression equation made by analysis of variance (ANOVA) shows the empirical relationship among the target variables (ammonia removal) and the three operating conditions or variables. The equation in terms of coded factors is represented by Eq. (10).

Final equation in terms of coded factors:

$$\text{Ammonia removal} = 93.56 + 17.47 \times \text{Mg: } NH_4 + 8.87 \times PO_4{:}NH_4 + 10.13 \times \text{pH} + 2.66\ (\text{Mg: } NH_4 \times PO_4{:}NH_4) - 3.11\ (\text{Mg: } NH_4 \times \text{pH}) + 1.81\ (PO_4{:}NH_4 \times \text{pH}) - 10.23\ (\text{Mg: } NH_4)^2 - 6.55\ (PO_4{:}NH_4)^2 - 12.33\ (\text{pH})^2 \quad (10)$$

The high significance of the model was also established in the plot of calculated values against the experimental values of ammonia removal % (Figure 3). Figure 4presents the response surface modelling in a three dimensional representation reflecting the effects of molar ratio $Mg:NH_4^+$, $PO_4^{-3}:NH_4^+$and pH on the ammonia removal after two hours of reaction. As a general trend, it was observed that effects of molar ratio $Mg:NH_4^+$ and $PO_4^{-3}:NH_4^+$ on removal of ammonia was pH-dependent. At low (≤ 7) or very high pH (≥ 10.5), is very difficult to precipitate ammonia into struvite. At high pH, Mg is converted into $Mg(OH)_2$ or $Mg_3(PO_4)_2$ salt.

Characterization and Identification of Struvite

The morphology of the precipitated crystals obtained during ammonia removal by optimized value (by RSM) of molar ratio $Mg:NH_4^+$, $PO_4^{-3}:NH_4^+$and pH was characterized by XRD and SEM-EDX analysis. Microphotography and elementary chemical composition of amorphous precipitates (struvite) were determined by using SEM-EDS. SEM image analysis indicated that the size of the crystal was non-uniform (40-60 μm length). EDS analysis showed that the surface composition of the precipitates contained high amounts of O, P, and Mg small peaks corresponding to sulphur, potassium and iron have also been identified. The XRD pattern of powdered form of struvite matched very well with that of the published pattern for struvite. The XRD analysis indicated that the prominent characteristics peaks of the precipitate were similar to that of the pattern of MAP standard (JCPDS 15-0762).

The TGA curve was converted into its derivative mode (DTGA) from the rate of mass loss curve as a function of temperature. As indicated by the data at temperature around 55°C mass loss begins and is really complete when the temperature reached above 250°C. At this temperature, about 52.2% of the original mass loss occurs. The following decomposition reaction for struvite shows the mass loss (Eq.11):

$$MgNH_4PO_4.6H_2O \rightarrow MgHPO_4 + NH_3\uparrow + H_2O\uparrow \quad (11)$$

A single peak was found which is attained at temperature 102^{0}C for DTGA curve of struvite at heating rate 10^{0}C per minute. The single peak indicates to major mass loss during the entire course of heating.

The FT-IR spectrum for the struvite was also consistent with the published IR spectrum of struvite in the wave-number range of 500-4000 cm^{-1}, with 100% recovery of spectra according to the standards as shown in part a of Figure 8.The Fourier transform infra-red spectrum of struvite showed that the infrared spectrum of the precipitate was close to that of the MAP as reported elsewhere [He, et al.(2007)]. At 3361-2915 cm^{-1} water-stretching broad band was observed which indicated the presence of crystalline hydrate which was absent after TGA treatment. The water-phosphate hydrogen bonding was attributed to 2345 cm^{-1} band. The FT-IR spectrum of struvite displays a set of bands at 1690, 1440 and 1340 cm^{-1}. The band at 1690 cm^{-1} assigned to the HOH deformation of water, other two bands 1440 and 1340 cm^{-1} to the HNH deformation modes of NH_4 units. These bands are not present in the thermally treated struvite as shown in the Figure 5. The other band at 1010 cm^{-1} is ascribed to the water NH_4 rocking modes. This bands are absent after thermal treatment. Two bands at 615 and 578 cm^{-1} were observed in the infrared spectrum and are assigned to the υ_4 bending modes of the PO_4 units. After thermal treatment, these bands were observed at 824 and 580 cm^{-1}.

Nanofiltration: The Final Polishing Step

Ammonia removal through MAP precipitation resulted in increased values of TDS, salinity and conductivity due to introduction new ionic species and salts in the solution. Cyanide, phenol and remaining ammonia and COD were also present in the wastewater after ammonia precipitation. Microfiltration could only remove particle size bigger than 0.45µm like struvite, but not the ionic species which should be removed prior to its disposal to any water bodies. Nanofiltration played a significant role in removal of these phenolic intermediate compounds (COD), ionic species and salts in the final stage of treatment of coke wastewater. Polyamide composite nanofiltration membranes (NF1) fitted in a largely fouling-free cross flow module was examined during nanofiltration at optimized pressure 16 bars and cross flow rate 800 L/H. At pH values >7.0, most of the polyamide composite nanofiltration membranes possess negative zeta potential. The pH of feed solution was maintained 10.0, so that all pollutants like cyanide, phenol etc exhibited the negative charge.

CONCLUSIONS

The study demonstrates that for struvite recovery, a by-product from industrial ammoniacal wastewater. By appropriate integration membrane-based treatment with conventional chemical treatment the treatment plants could be turned operationally fast, economically more viable and environmentally more benign. However, chemical treatment units for struvite precipitation should be operated under well optimized conditions where rigorous experimentation using response surface methodology could be of great help to reduce the chemical contamination in the form of TDS, conductivity and salinity. In this experiment pH of the wastewater was chosen around 10.0 during treatment which was the natural pH of the feed. Future studies should explore raising scale up confidence for struvite production through modelling and simulation.

ACKNOWLEDGEMENTS

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REFERENCES

Battistoni, P., Paci, B., Fatone, F. and Pavan, P. (2005) Phosphorus Removal from Supernatants at Low Concentration Using Packed and Fluidized-Bed

Reactors.Ind. Eng. Chem. Res., Vol. 44, pp. 6701-6707.

*Doyle, J.D. and Parsons, S.A. (**2002**) Struvite formation, control and recovery. Water Res., Vol. 36, (16), pp. 3925–3940.*

*Han, M., Li, G., Sang, N. and Dong, Y. (**2011**) Investigating the bio-toxicity of coking wastewater using Zea mays L. assay.Ecotoxicol. Environ. Saf.,Vol. 74, pp. 1050-1056.*

*Hameed, B.H., Tan, I.A.W. and Ahmed, A.L. (**2008**) Optimization of basic dye removal by oil palm fibre based activated carbon using response surface methodology. J. Hazard. Mater.,Vol. 158, pp. 324–332.*

*He, S., Zhang, Y., Yang, M., Du, W. and Harada, H. (**2007**) Repeated use of MAP decomposition residues for the removal of high ammonium concentration from landfill leachate, Chemosphere, Vol. 66, pp. 2233–2238.*

*Kumar R., Bhakta, P., Chakraborty, S. and Pal, P. (**2011**) Separating Cyanide from Coke Wastewater by Cross Flow Nanofiltration. Sep. Sci. Technol., Vol. 46, pp. 2119–2127.*

*Liikanen, A.; Martikainen, P.J. (**2003**) Effect of ammonium and oxygen on methane and nitrous oxide fluxes across sediment-water interface in a eutrophic lake. Chemosphere, Vol. 52 (8), pp. 1287–1293.*

Myers, R.H. and Montgomery, D.C. (1995) Response Surface Methodology: Process and Product Optimization Using Designed Experiments, 1st Ed.; John Wiley & Sons Inc.: New York.

*Stratful, I., Scrimshaw, M.D. and Lester, J.N. (**2001**) Conditions influencing the precipitation of magnesium ammonium phosphate. Water Res., **Vol.** 35 (17), pp. 4191–4199.*

Silva, J.P., Sousa, S., Goncalves, I., Porter, J. and Ferreira Dias, S. (2004) Modelling adsorption of acid orange 7 dye in aqueous solutions to spent brewery grains. Sep. Purif. Technol., Vol. 40, pp. 163–170.

Standard Methods for the Examination of Water and Wastewater, 19th ed.; (1995) American Public Health Association/American Water Works Association/Water Pollution Control Federation: Washington, DC.

*Wang, B., Chang, X. and Ma, H. (**2008**) Electrochemical Oxidation of Refractory Organics in the Coking Wastewater and Chemical Oxygen Demand (COD) Removal under Extremely Mild Conditions. Ind. Eng. Chem. Res., Vol. 47, pp. 8478–8483.*

Table 1. Characteristics of raw industrial wastewater (coke-oven)

Parameters	Concentration (mg/L)
pH	9.5
Ammonia	3450
COD	3345
TDS	23820
Phenol	75
Thiocyanate	141
Cyanide	45
Conductivity (mS/cm)	11.2
Salinity	8.1
Oil & Grease	48

Table 2. Values of C_e, K and R^2 obtained at different molar ratio ($Mg:NH_4:PO_4^{-3}$)

Molar ratio ($Mg:NH_3:PO_4^{-3}$)	C_e (mg/L)	K (min^{-1})	R^2
3:1:1	304	0.0284	0.984
1:1:2	437	0.0258	0.972
1:1:0.5	798	0.0246	0.985
0.5:1:1	1189	0.020	0.996

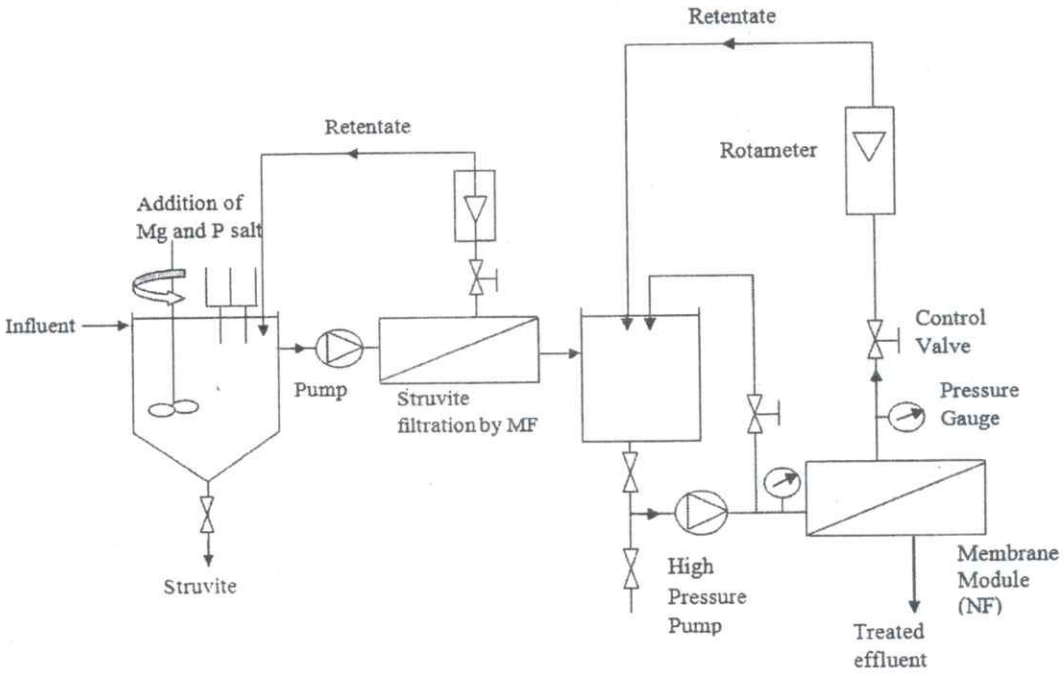

Figure 1 A detailed schematic of the experimental set-up

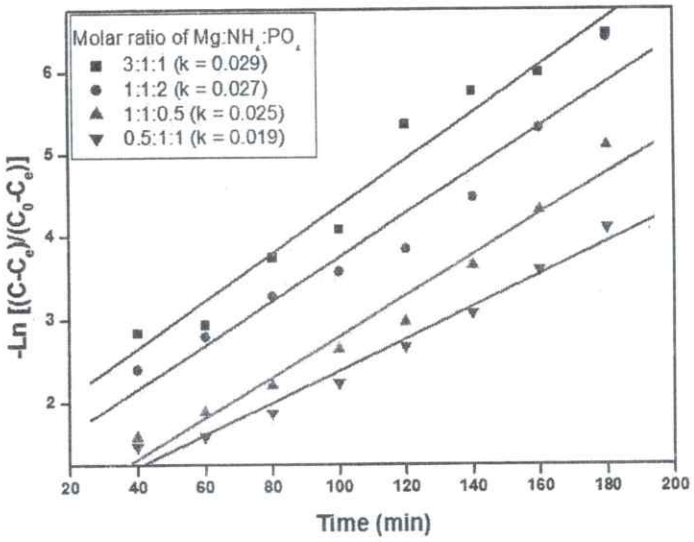

Figure 2 Linearization of the first-order kinetic equation for determining the kinetic constants at different molar ratio at pH 9.0

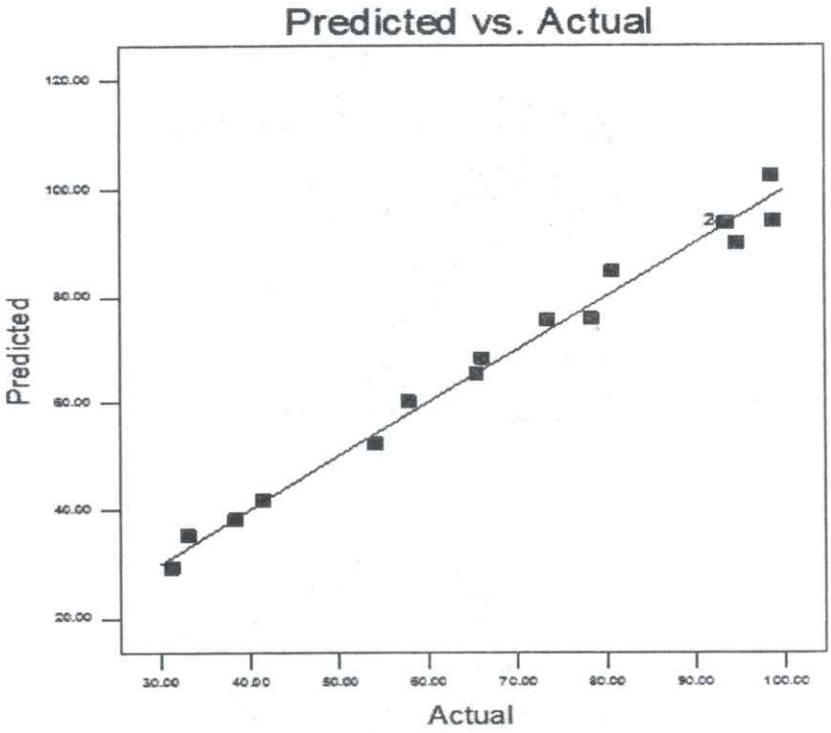

Figure 3 Distribution of experimentally determined values versus statistically predicted values of ammonia removal (%)

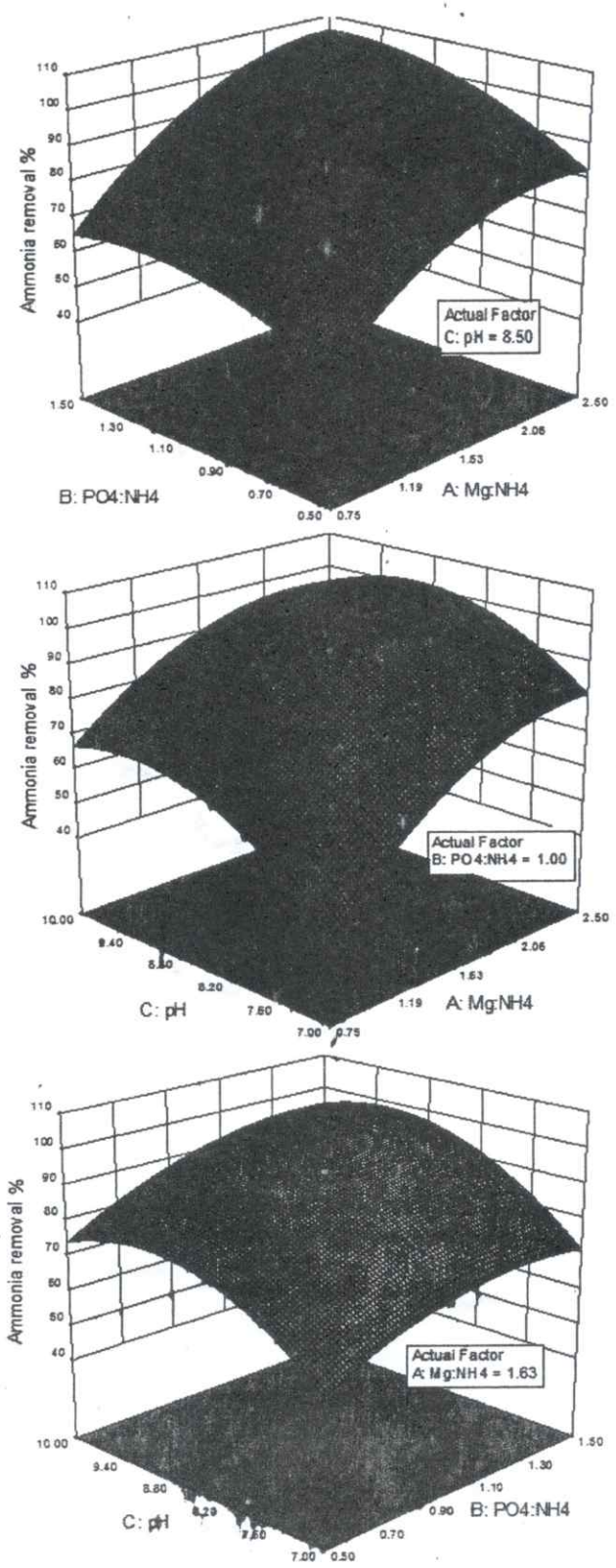

Figure 4 Response surface plot showing the removal % of ammonia (A, B, C) with variable parameters molar ratio of $Mg:NH_4$ and $PO_4^{-3}:NH_4$ with pH.

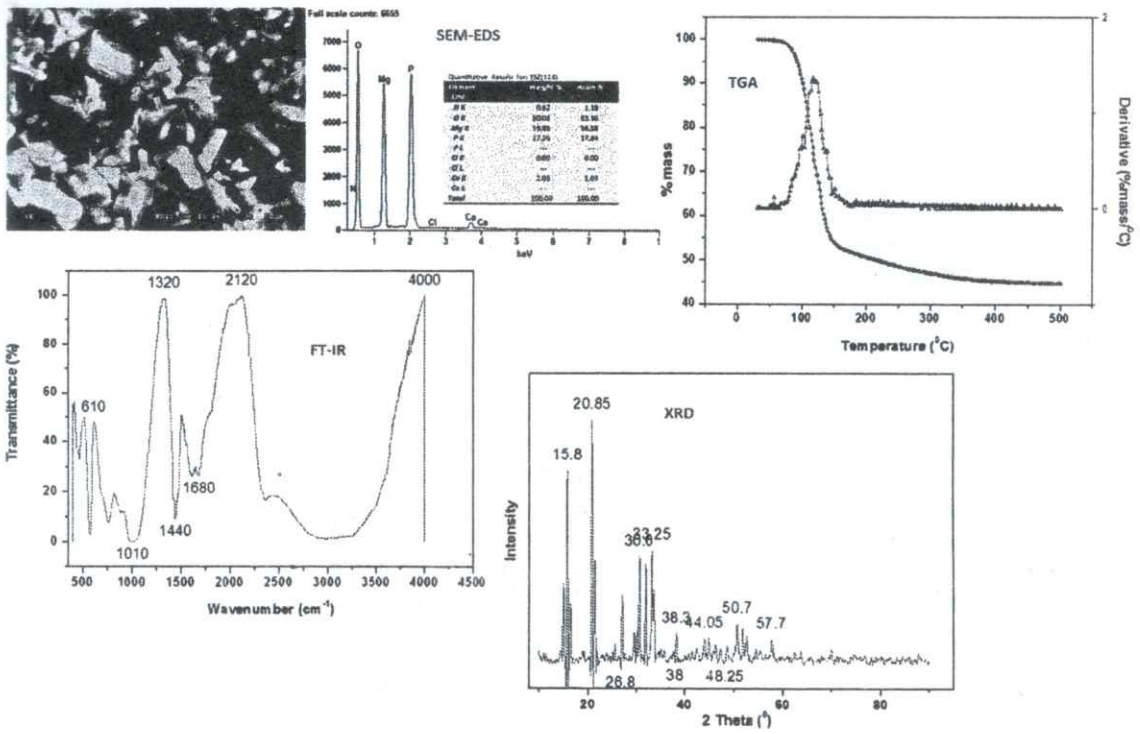

Figure 5 Surface characterization analysis of struvite (MAP) obtained during the chemical treatment of ammonia: (a) and (b) scanning electron microscopy analysis of struvite at two magnification; (c) XRD pattern of the struvite crystel (d) elemental composition analysis by SEM-EDS of struvite

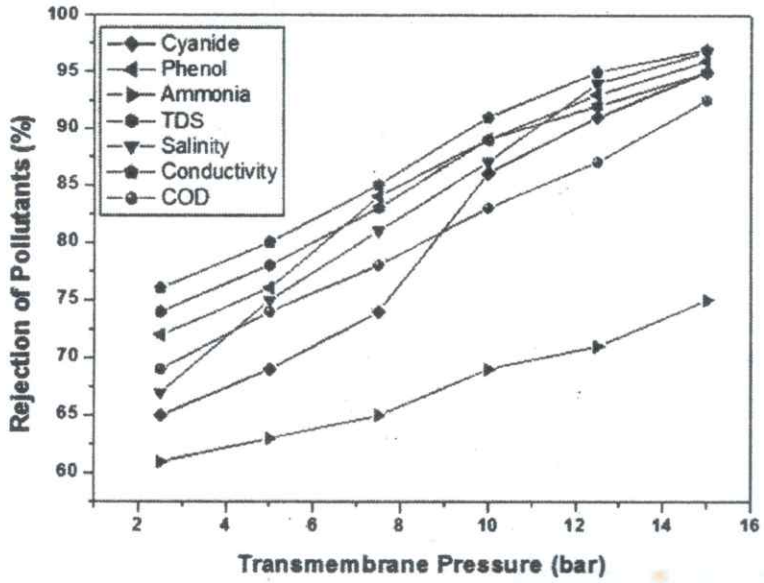

Figure 6 Effect of applied pressure on other pollutants rejection percentage for NF1 membrane. Operating conditions: transmembranes 16 bar, cross flow rate 800L/H, pH 9.5 and temperature 35^{0}C.

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COAL BED METHANE: WASTE TO WEALTH

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ABSTRACT

The increase in demand of energy and growth of modern industrialisation is in exponential rate. Environmental scenario therefore is a major concern. Attention is diverted towards the cleanest burning fuel among which coal bed methane is one. This is also known as natural gas in coal (NGC). Methane gas extracted from coal seam is named as coal bed methane (CBM). The major constituent of coal bed methane is methane. It requires minimal processing before it is put to use. It is generated during the coalification process and either absorbed into coal substrate or remains as free gas in fractures of coal bed. Coal bed methane is versatile and has the potential to replace much coal based fuel. It is produced at very low pressure. The production process consumes very less water. It is an environmentally benign fossil fuel in the form of gas which is compressed and transported through pipeline either for domestic or for industrial purpose. It emits 30-50 % less carbon dioxide than the coal fired power plants which, if left as such will add to global warming problem and wastage of cleaner energy. In opencast coal mining CBM is released to the atmosphere and is a waste. Capturing CBM through drill holes and pipeline combination has gathered enormous pace before the coal seam is actually exploited by underground mining. Coal seams at greater depth cannot be mined but CBM can be recovered through drilling for use.

KEY WORDS: Methane, Coal Bed Methane, Natural Gas, Green House Gas, CDM.

INTRODUCTION

Coal bed methane is found along side coal from the remain of plants and animals buried million of years ago and trapped in fractures of coal. Methane (CH_4) is a gas formed as part of the process of coalification. When coal is mined methane is released from the coal seam and the surrounding disturbed rock strata[1]. Methane can also be released as a result of natural erosion or faulting. Coal bed methane travels with ground water in the coal seams.

Generally, methane content in coal seams increases with depth and age. As the depth of the coal seam increases, so does the pressure level[2]. This in turn reduces the level of permeability, causing the methane to be much more tightly bound to the coal and surrounding rock strata. Underground mining can therefore produce substantially greater levels of methane than surface mining. In fact, underground mines account for the majority (up to 90%) of all methane emissions from the coal sector.

Depth Interval (Mtr)	Mean methane content (M^3/ton of coal)	Depth Interval (Mtr)	Mean methane content (M^3/ton of coal)
100	0.02	1500	4.89
500	0.99	2000	7.09
1000	3.73	*Source: IEA CCC 2005*	

Methane is highly combustible – its release can have serious implications for the safety of mine operations. It is also a potent greenhouse gas (GHG)–23 times more harmful than carbon dioxide (CO_2). Tackling methane emissions is therefore an important step in meeting the challenge of climate change and in ensuring the

safety of mining operations. Methane can also act as a valuable source of energy- it is the principal constituent of natural gas.

ENVIRONMENTAL IMPACT OF COAL BED METHANE

Methane is released during the process of extracting coal in both surface and underground mining. The released methane then mixes with air, which becomes highly explosive if methane concentration levels reach 5-15%. Methane explosions are devastating, causing significant loss of life and damage to property. The risk of explosion is a particular problem in underground mines, where providing a sufficient level of ventilation air is essential. Failure to provide enough air to dilute the methane below the 5-15% range can put miners at risk due to the threat of explosion. In surface mining, the released methane is heavily diluted by its immediate exposure to air and therefore the risk of explosion is minimal. In order to prevent the wastage of methane the recovery technologies have been improved and deployed on a wider scale.

Coal mining is an important anthropogenic source of methane emissions[3]. Although agriculture accounts for by far the largest proportion of methane emissions from human activities, emissions from all coal mining related activities - extraction, transport and storage-accounted for around 8% of total global anthropogenic methane emissions in 2006. The global warming potential (GWP) of methane is 23 times greater than that of CO_2. Methane has a relatively large global warming effect over a short period of time, whereas CO_2 has a relatively small global warming effect but over a much longer period of time[4].

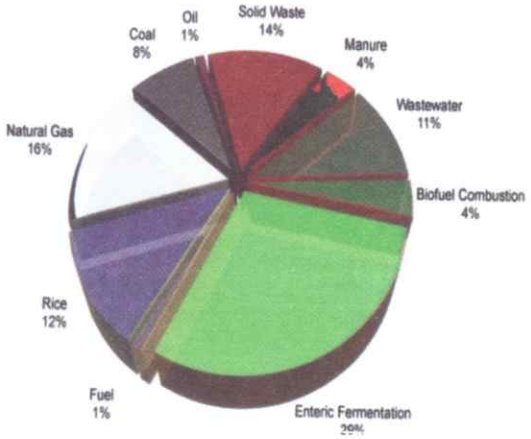

Fig No.1 Global Methane Emissions from Human Activities (2006), *Source: M2M 2006*

TRANSFORMING WASTE TO WEALTH

The recovery of methane released during coal mining plays an important role in global efforts to reduce GHG emissions and mitigate climate change. Methane is one of five greenhouse gases covered by the Kyoto Protocol and this provides opportunities for countries to meet their obligations under Kyoto by undertaking projects that reduce methane emissions from coal mining activities. These projects can be developed domestically or in host countries under the Protocol's Clean Development Mechanism (CDM) and Joint Implementation (JI) scheme.

Methane is a valuable energy resource; 70-90% of natural gas is methane[5]. Coal seam methane provides a useful 'unconventional' source of natural gas. The resources are distributed differently to

the 'conventional' natural gas found in natural gas fields. This allows countries with restricted access to natural gas but plentiful coal supplies to utilise alternative sources of natural gas. Coal seam methane (>93% concentration) can be fed into the existing gas pipeline network to supplement or replace conventional natural gas. Coal seam methane can also be utilised to replace or supplement conventional natural gas in electricity generation systems such as gas turbines and gas engine systems. These systems are often deployed directly on mine sites to provide auxiliary power to the mines themselves.

COAL BED METHANE IN INDIA

India initiated evaluating its coal bearing basins for their coal bed methane potential in 1992. In a short span of five years it tested and flowed coal bed methane from one of the coal seams of Barakar Formation in Jharia basin[2]. In 1997 India tested and flowed coal bed methane for the first time from a well drilled in the Parbatpur block of Jharia basin[6]. India's CBM production is estimated to reach 4 million standard cubic meters per day (mscmd) by 2016-17, as compared to the current level of 0.23 mscmd in 2011-12.

TECHNOLOGIES AVAILABLE

A range of technologies are available to recover methane from coal and these can be placed under three categories.

(1) **Coal Bed Methane (CBM):** Methane recovered from un-mined coal seams. The coal seams may be mined in the future but this is largely dependent upon geological factors such as coal depth and quality. Methane is recovered from un-mined coal seams for two primary reasons:

- It may be necessary to drain the seam of as much methane as possible before mining takes place. This reduces the risk of explosion and mitigates methane emissions to the atmosphere once the process of extracting the coal begins.
- The methane may be recovered for its energy production potential, regardless of whether the coal will actually be extracted.

The potential for future mining operations is largely dependent on the accessibility of the coal seams. Coal found at extremely deep depths is often not considered feasible for extraction because of practical, safety and economic considerations. In such cases, methane recovery activity is purely for the purpose of energy generation and does not have safety or climate change benefits.

(2) **Coal Mine Methane (CMM):** Methane recovered during mining activities as the coal is in the process of being extracted and thus emitting significant quantities of the gas.

(3) **Abandoned Mine Methane (AMM):** Methane recovered from mines that have been abandoned following the completion of mining operations. Significant amounts of methane may remain trapped in the mine or may continue to be emitted from openings[7].

RECOVERY TECHNIQUES

Exploration of coal bed methane begins with mapping of coal seams. Coal seams are assessed using a single vertical well however in some areas a lateral well may be made to increase the gas gathering area. In the case of seams at shallow depths, vertical wells have been traditionally used. These vertical systems often use layers of fracture wells, which drain the methane from fractures in the coal seam produced as result of the increased pressure created during the dewatering process.

Horizontal drilling techniques may be used in case of virgin coal bed methane (VCBM) for increased accuracy and flexibility. Within these horizontal systems, flow enhancement techniques such as extra hydraulic fracturing - where water is pumped into the seam at high pressure - may be deployed to further facilitate the release of the methane from

coals seams. Horizontal systems can recover much higher volumes of methane from coal seams at extreme depths than a vertical system but the recovery efficiency is relatively low and heavily dependent on the overall length of the drill through the coal seam.

Extracting the gas begins with a drilling and stimulation of coal seams to open the pores within the coal. This production zone releases the pressure within the coal bed and allows the gas and water to flow into the well and then to the surface through pipes. Water is transported through underground pipes to a pool for recycling. Gas is transported to a processing facility for compression and dehydrated. Concentration levels of methane recovered via these techniques can often exceed 95%, making the gas suitable for use as a direct replacement for conventional natural gas in pipeline networks. Then the gas can be sent through pipe lines to domestic or commercial markets.

CONCLUSION

Once considered and allowed to be wasted is the most acceptable form of fossil fuel now. Even at present almost all the coal bed methane is diluted and released to the atmosphere during opencast coal mining. The extraction of coal bed methane needs to be monitored and managed. The quantum of impact on environment may vary depending upon the geological condition and recovery technique. The most important thing is methane is much cleaner than coal. With growing demand and rising oil and gas prices, CBM is definitely a viable alternative energy source. Moreover, CBM extraction also potentially offers the opportunity of earning carbon credits under Clean Development Mechanism of Kyoto Protocol, being an environmentally friendly fuel. Coal bed methane will clearly emerge as the one of the viable and clean routes to India's energy security.

REFERENCES

1. *C.F.R.I.: "Indian Coal Quality Evaluation Data". Vol 2, Jharia Coalfield, Dhanbad (1979).*
2. *Chandra, Kuldeep, Sahai,S, Awadesh Rai, Debashis Das, U.K.Gupta and A.K.Singh,: " Coal bed Methane Resources of India – A Case Study Of Jharia Basin" Petrotech, 99 Vol IV (199).*
3. *Kelafant, J.R.: "A Review of Global Coalbed Methane Resources and Activity." Indian Jour. of Pet. Geol. (In Press, 2000).*
4. *Lamberson, M.N. and Bustin, R.H.: "Coalbed Methane characteristics of the Gates Formation, British Columbia: Effect of Maceral Composition." A.A.P.G. Bull. 77 (2) (1993).*
5. *Meissner, F.F.: "Cretaceous and Lower Tertiary coals as source for gas accumulation in Rocky mountain area." In "Source rocks of Rocky Mountain Regions", Rocky Mountain Assoc. Geol. Guide Book (1984).*
6. *Punjrath, N.K., et.al: "Identification of Probable CBM Prospects and Fairways in Parbatpur Block – Jharia Basin" Un pub. ONGC Report (1997).*
7. *Sengupta, N, "A revision of the Geology of Jharia coalfield with particular reference to distribution of coal seams." Ph.D. Thesis, Indian School of Mines, Dhanbad (1980).*

➢ SGAT NEWS

- National Seminar on **Mining and Community Welfare** was held on 22 & 23 September 2012 at Hotel Crown, Bhubaneswar, jointly with Geological Society of India (GSI).

- Students' interaction meet was held in SGAT Hall on Oceanic atmospheric and earth resources on 24th Sept'2012. 14 schools with 100 students were present. The programme was organized jointly by SGAT and Geological Society of India (GSI).

- AGM of Geological Society of India was held in Conference Hall of SGAT on 23rd Sept'2012. Dr. Harsh K. Gupta, President and Mr. R.H. Sawkar, General Secretary of Geological Society of India were present.

- A National Seminar on on Waste to Wealth is held on 14-15 December 2012 in SGAT Building organsied jointly by IIM, Bhubaneswar Chapter and SGAT.

- 32nd Annual General Body Meet was held on 15th December 2012 at SGAT Hall. In this meeting Dr. Virendra Kumar Singh, CIMFR has been awarded with SGAT Award of Excellence – 2012, Dr. Niranjan Behera, Sambalpur University has been awarded with Smt. Veena Roonwal Memorial Award - 2012 and Dr. R.C. Mohanty, Dr. S.K. Sarangi and Er. Ghanashyama Khuntia, FIE have been awarded with SGAT Life Time Achievement Award – 2012

- SGAT has prepared and submitted a Memorandum to Hon'ble Justice M.B. Shah Commission highlighting various mining issues and controversies happening in mining scenario of Odisha. Memorandum was submitted on 10.11.2012 at Bhubaneswar.

- Mineral Development Awareness Quiz (MDAQ) – 2012 was organized by SGAT from 17-19 August 2012 at Joda Valley Club at Tata Steel. As many as 15 teams from IIT, Kharagpur, Jadavpur University, ISM-Dhanbad, Utkal University, BESU-Sibpur, Sambalpur University, Andhra University, NIT-Rourkela, Govt. College of Engineering, Keonjhargarh, IGIT – Sarang, D.D. College, Keonjhargarh participated in the programme. Deptt. Of Metallurgical and Materials Engineering of Govt. College of Engineering, Keonjhargarh represented by Shri Ranjan Kumar Mohanta and Ms. Puspa Gautam was adjudged as the overall best team. The programme was supported by Tata Steel, EMIL, Rungta Group of Mines, OMC Ltd. and EZMA.

- SGAT organized a meeting on 18th Aug'2012 in the Joda Valley Club, Joda to review the recommendations made in the Seminar on Approach and Strategy for Integrated Development of Joda-Barbil-Koira mining area. The review meeting focused on technology, environment, management, infrastructure development, approach roads to railway stations, water supply, railway, health care, sports, education, mining, CSR and employment.

- **State Level Environment cum Mineral Awareness Programme (EMAP)-2013 held on 2 & 3 February 2013 at Bhubaneswar**

Record of Proceedings

As a part of continuing efforts to promote awareness and action plan for restoration of greenery, creation of pollution free environment and highlighting importance of minerals in economic development, **Society of Geoscientists and Allied Technologists (SGAT)** has been organising EMAP in the major mining regions of the State on annual basis for

over 22 years. The participants are students of Higher Secondary schools.

The Regional Programmes were held during the period, November 2012 - January 2013. The following 10 schools who emerged winners participated in the State Level EMAP.

(1)Kerala Public School, Rairangpur, (2) Nirmala English School, Rajgangpur, (3) DAV School, Unit -8, Bhubaneswar, (4) St. Xavier's High School, Ambapua, Berhampur, (5) Ispat High School, Kalta, (6) DAV School, Noamundi, (7) Dhabalgiri High School, Jajpur Road, (8) Saraswati Vidya Mandir, Brajrajnagar, (9) DAV Public SchoolMCL, Kalinga Area, Talcher, (10) Delhi Public School, Damanjodi

The State Level Programme consisted of the following activities:-

i. Visit to Regional Museum of Natural History, Pre-historic Life and Science Park, and Bhubaneswar Meteorological Centre.
ii Identification of Mineral Specimen, Plant Specimen, Photographs of Personalities, Places, Mining equipment and natural disasters
iii. Written Test
iv. Elocution
v. Exhibition of Documentary Film on "Mining and Environment" made by SGAT
vi. Oral Quiz

The activities (i) to (vi) were organised at SGAT building.

Delhi Public School, of Damanjodi represented by S/Shri Sanskar Sahoo and Sumit Kumar Pradhan was adjudged the overall best team in the 2013 State Level EMAP. DAV School, Unit - 8, Bhubaneswar and DAV Public School, MCL Kalinga Area emerged as the 2nd best and 3rd best teams respectively. Sri Kaushik Pandey of DAV Public School, Noamundi, secured the highest marks in the written test.

The organisations who had contributed to the success of the programme at the Regional and State levels include Tata Steel, JSPL Rungta Mines, SAIL, OMC, MCL, OCL India, NALCO, Sarda Mines, M/s G.S. Mishra, OSCOM, MGM Group, M/s. S.N. Mohanty, EMIL, Patnaik Minerals, Misrilal Mines, Balasore Alloys, FACOR, IMFA, EZMA among others.

Admirable assistance was available at the field level from Dr. U C Jena, Shri Ballabh Chandra Nayak, Shri S N Sahu, Deputy Directors of Mines, Joint Directors of Geology Shri S N Parida and Shri S K Padhi, Mining Officers Shri S K Behera and Shri B. Mahanta.

The various tests of the State Level Programme were evaluated by Sm. Sushree Jena, Shri T. Mahanta, Shri Subhransu Mishra & Shri J.P. Behera of Directorate of Geology, Shri Rabi Mohapatra & Shri S.P. Mishra of Geomin have designed the Quiz Programme for power point presentation. Shri T. Mahanta, Joint Director of Geology conducted the power point presentation. Dr. V.P. Upadhyay, Director, MOEF was the Quiz master. Prof. N.K. Mahalik had evaluated the written test answers Dr. T. Basa of OMC did the scoring Shri J.K. Hota & Shri B.C. Pattnaik coordinated and supervised the Regional EMAP of Talcher and Ib Valley areas.

The programme had the distinguished presence of Prof. M.C. Dash, Prof. G.B. Mishra, Prof. S. Acharya, Dr. V.P. Upadhyay, Dr. S.C. Sahoo (Director, Meteorological centre), Prof. N.K. Mahalik Prof. Madhumita Dash, Shri P.K. Panda, Shri Ardhendu Mahapatra and Shri Nihar Das Pattanaik of EMIL, Shri Sushant K. Mishra of Tata Steel, Dr. Sugata Kar (former CDMO, Capital Hospital) Dr. S.N. Patra of Odisha Environment Society, Shri R.C. Samal, Shri G.B. Mahapatra, Dr. U C Jena among others.

Prof. M.C.Dash, Prof. N.K. Mahalik and Dr. V.P. Upadhyay constituted the jury for the elocution programme.

Dr. V.P. Upadhyay addressed the students and their teachers and complimented SGAT for organising such a wonderful programme year after year. He called upon the teachers to be proactive and take initiative for protection of our environment and motivate the students to be a part of the campaign to make our surrounding pollution free **Dr. S.K. Sarangi,** President, SGAT thanked the students for participation and taking active interest in the various activities organised by SGAT, members of SGAT and organisations who have extended support for success of the event. He observed that this is a unique programme at merits involvement and support of all sections of the society.

The students were presented jersey with the emblem **"Go Green - SGAT"** and the schools were gifted Mineral Set Boxes. All the participating students were presented with gifts and certificates. The programme both at the regional and State Level was designed, coordinated and supervised by **Shri B.K. Mohanty**, Adviser, SGAT.

- **FORTHCOMING EVENTS OF SGAT**

Mineral Development Awareness Quiz (MDAQ) – 2013: The programme designed for University level students for Geology, Geophysics, Mining Engineering, Metallurgical Engineering, Environmental Engineering would be held sometime in August – September 2013.

Environment-cum-Mineral Awareness Programme (EMAP) – 2013: The programme would be organized for IXth class students from October-December 2013 followed by State Level EMAP in January/February 2014.

Workshop: One day workshop on "Water Management in Bhubaneswar area" would be organized in September 2013.

Seminar: A seminar would be organized in December 2013. The theme/topic of seminar will be finalized by E.C. shortly.

Training Programme: Imparting condensed course on geology, mining, environment, surveying to the professionals of mining industries would be taken up.

➢ **NEWS ABOUT MEMBERS**

- Sri Ganesh Mohanty, JDM retired from Govt. service on 30.06.2012 on attaining the age of superannuation.
- Dr. D.K. Mishra, JDM and Mr. P.C. Patra, DDM retired from Govt. service on 31.07.2013 on attaining the age of superannuation.
- Dr. B.K. Mohapatra, Scientist, IMMT got extension w.e.f. 01.04.2012 for 2 years after superannuation.
- Mr. T. Mahanto, JDG (L-II) and Mr. A.K. Mohanty, JDG (L-II) got promotion to the post of JDG (L-I) in Nov'2012.
- Dr. B.M. Faruque, Director (Retd.), GSI, participated in an International Conference on IGCP588 on Changing Shorelines, held at Kiel in northern Germany during 5-10 Sept'2012.
- Prof. M.C. Dash published a book titled "Charles Darwin's Plough – Tools for Vermi Technology (185 pages) through IK International Publishers, New Delhi in 2012. He delivered the prestigious Prof. Ramdeo Mishra Birth Centenary Lecture on 26th Dec'12 n the Auditorium Hall of Regional Museum of Natural History, Bhubaneswar after being felicitated by National Institute of Ecology.
- Prof. (Dr.) Golak Bihari Misra received Prf. S.K. Bose Memorial Award for 2011-12 for excellence in teaching in Mining Engineering. The award was received by him at 106th Annual General Body Meeting of MGMI.
- Mr. P.C. Vajani retired from Govt. service on 31.01.2013 on attaining the age of superannuation.

- **NEW MEMBERS**

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OBITUARY

Naba Kishore Das
(1934-2012)

N.K.Das was born to a family of freedom fighters at a village near Nilgiri, Odisha on 14 July 1934. He had his earlier education at Nilgiri High School and Balasore College. Very few of his friends knew that he had to serve as a teacher to meet his educational expenses. Later he studied at Asutosh College, Kolkata. He was staying in a small hotel at Hazra Road, where I met him for the first time. N K Das joined Patna University from where he completed his M. Sc. in Geology in the year 1957. After passing out, he joined Keonjhar Science College as a lecturer in Geology where he was spotted by Shri Niranjan Pattnaik, currently President of Odisha Pradesh Congress Committee. This was followed into wedlock with the daughter of Late B D Patnaik of Keonjhargarh, one of very few Odia mine owners of the State. I had attended his marriage at Keonjhargarh and his marriage reception at Nilgiri. After a brief stint as a lecturer at Keonjhar Science College, Das joined Directorate of Mining & Geology, Government of Odisha as a Geologist. He rose to the rank of Joint Director of Geology (Level-I). One of his important investigations was determination of foundation condition of the proposed Aero Engine factory at Sunabeda. By far, his distinctive achievement was shaping the activities of ORSAC to a national level. He was with ORSAC for about 5 years. Right thorough his service career, N K Das made his mark as an honest and dedicated officer with innovative ideas. He had ready solution to all problems that were posed before him by his colleagues and superiors.

N K Das passed away on 23 December 2012 at Bhubaneswar after prolonged illness. He is survived by his wife, two sons and a daughter. His death is a personal loss to me. Sri N.K. Das was the founder member of SGAT and SGAT family will miss a devoted and conscientious member ever dedicated to promotion of mineral development of the State. SGAT conveys soulful condolence to the members of the bereaved family. May his soul rest in peace.

B K Mohanty, Advisor, SGAT
&
Members of SGAT Family

- **SUBMISSION OF PAPERS FOR SGAT BULLETIN**
  (Instruction to Authors)

Research papers, review articles, short communications, announcements and letters to editors are invited on topics like geosciences, mineral exploration, mining, materials science, metallurgy, mineral industry and trade, mineral economics, environment, education, research and development, legislation and infrastructure related to mining, mineral policy and mineral development planning.

Submission of manuscript implies that the same is original, unpublished and is not being considered for publication elsewhere. Two copies, complete in all respect (with copies of figures and tables) are required to be submitted. Originals of figures and tables should be enclosed separately. Each manuscript must accompany by a computer diskette (floppy) containing the electronic version of the text. Electronic files of figures, if available, should be submitted in a separate diskette. In each case, the details of software and type of equipment used should be clearly indicated. The copies of manuscripts, strictly in accordance with the instructions to authors given below may be sent to the editor of the bulletin.

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(d) Books should be referred to as: Sengupta, S.M. (1994) Introduction to sedimentology. Oxford and IBH Publ. Co. Pvt. Ltd., New Delhi, 314 pp.

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