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PLANNED UTILIZATION OF RAW MATERIALS FOR BASIC REFRACTORIES*

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High temperature furnaces for matallurgical industries, particularly those for iron and steel manufacturing process, are the principal consumers of the basic refractories. Availability and quality of the raw materials are essential factors for producing high grade refractory products required for high temperature furnaces. In this paper, present status of raw materials, like magnesite, chromite, dolomite, for basic refractories and their future demand and outlook in India, have been discussed. Planned utilization of the existing raw materials is the only way for maintaining production of required quantities of different types of refractories. In this connection, possibilities of beneficiation of magnesite and chromite and manufacturing of refractories from alternate sources of raw materials are examined.

Key Words : Basic Refractories; Magnesite; Sea-Water Magnesite; Chromite; Dolomite

INTRODUCTION

HIGH temperature furnaces for metallurgical industries like iron and steel, copper, lead, zinc and alumina are the principal consumers of the basic refractories. Out of these, iron and steel industry is the most important one. About 70 per cent of the refractories produced in India are consumed by the iron and steel industry. Steel plants in India take up over 90 per cent of the basic refractories produced in the country. From this it is obvious that the over-all-level of steel production controls the aggregate level of demand for basic refractories. The technology adopted in the iron and steel plant determines both the type and quality of refractory products needed and consequently there is no wonder that decision taken within the steel industry sets the trend of production and development of basic refractories.

Total requirements of refractories by an integrated steel plant normally comprise of 70 per cent fireclay and high alumina, 20 per cent basic and 10 per cent silica. The estimated demand for basic refractories for 1984–85 and 1989–90 based on the present practice and the future steel making techniques, and also considering the projected steel production of the country as indicated by the Working Group on Iron and Steel Industry set up by the Planning Commission in 1980 is shown in Table I.

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TABLE I

Demand for basic refractories in India for the year 1984-85 *and* 1980-90

(Projected steel production : 1984-85 = 15 million tonnes; 1989-90 = 22 million tonnes)

Consumers	Estimated demand (in thousand tonnes)	
	1984-85	1989-90
Steel plants	151	198
Other Industries	15	20
Export provision	15	25
Total :	181	243

With the adoption of modern process technology aiming at higher production and better quality, particularly in iron and steel industry, there appears to be a constant necessity for developing progressively better refractory materials to withstand the continuously increasing severe conditions in the industrial furnaces. The recent changes in the steel technology have created a demand for refractories with very stringent specifications. Besides the availability of adequate quntity of the raw material, its quality is an essential factor for producing quality refractory products. It is needless to emphasize that even the best technological know-how and modern plant and machineries would not be of any use, unless suitable material is available.

PRESENT STATUS OF RAW-MATERIALS

Magnesite and chromite constitute the primary raw materials for the manufacture of different types of basic refractories. With the introduction of L.D. process in the Indian Steel manufacturing process, refractory based on dolomite has also appeared in the scene. In this section, the requisite properties of the raw-materials for basic refractories and their availability in respect to refractory manufacturing processes are examined.

Magnesite

Magnesite is the most important source for basic refractory. It is to be calcined and sintered at high temperature to get periclase (Mgo), also known as dead burnt magnesite (DBM), which is subsequently used in the brick manufacture, either alone (Magnesite brick) or in combination with other refractory materials, mostly chromite in varying proportions—(Mag-chrome/chrome-magnesite). Apart from the natural source, synthetic magnesite (sea water magnesite) which is more pure than the natural one, is also widely used for the refractory purpose. Sintered magnesite is also used for fettling open hearth and electic arc furnaces and for the production of mortar, ramming mass and gunniting powders.

In India major workable deposits of magnesite are confined to Salem of Tamil Nadu and Almora-Pithorgarh area of U. P. The bulk of total in situ reserves of magnesite in India, has been estimated at 524 million tonnes, out of which total recoverable magnesite is 35.4 million tonnes only. At present, the annual production of magnesite is of the order of 371,000 tonnes. Refractory Industry accounts for about 95 per cent of the magnesium mineral consumption in India.

In Salem area the recoverable reserve is 27.4 million tonnes. Here the magnesite occurs as cryptocrystalline variety, formed due to alteration of magnesium-silicate minerals. It occurs as veins in the parent rocks and is associated with remnants of the latter. Consequently this magnesite is high in silica, which even goes up to 10 per cent. For manufacture of high grade basic refractories, SiO_2 content should be reasonably low in the dead burnt (DB) magnesite. As per the requirement of the I. S. Specifications, the SiO_2 content in D. B. Magnesite should not exceed 6.5 per cent in type I and 5.5 per cent in type II, a condition which can be fulfilled only if the SiO_2 content of the raw-magnesite does not exceed 2.5 per cent. Recovery of this grade from Salem is too low. Further it is found that in the D. B. Magnesite, meant for the L. D. Converters, the SiO_2 content should be preferably less than 0.5 per cent and the CaO/SiO_2 ratio sould be > 2. This shows clearly the limitation of our quality grade magnesite.

The magnesite deposit of Almora-Pithorgarh area is of coarse crystalline variety, formed by magnesium metasomatism of limestone/dolomite. Consequently this deposit is richer in CaO content and lower in SiO_2 content than the Salem deposit. SiO_2 content is generally low, and occasionally in some veins it is as low as below 1 per cent. However, it contains higher Fe_2O_3 content, generally above 2 per cent and lime content varies from 2–4 per cent. Although lower in SiO_2 the higher Fe_2O_3 and high content of CaO may pose a problem for its utilization in quality basic refractories.

Fortunately, the recently developed Khariduaga magnesite deposit of Nepal will also be available for Indian Refractory Industry. It is also a sedimentary deposit and fine to coarse crystalline in nature. This deposit is slightly purer than the Indian deposits, here SiO_2 varies from 1.5 to 2.5 per cent, Fe_2O_3 from 0.80 to 2.0 per cent and CaO only from 0.1 to 0.4 per cent. Total deposit in this area is estimated to be about 180 million tonnes out of which proved reserves of 11.75 million tonnes are of above quality.

Yearly production and export of magnesite for the period from 1975 to 1980 are given in Table II. It is found that production of magnesite in the country has remained more or less constant in the last decade. Further the purer quality of magnesite required to produce quality basic refractory is not available indigeneously. Refractory manufacturers are partly happy that the Government has approved import of purer quality Dead Burnt Magnesite.

Chramite

Chromite is used by blending in variable proportions with Dead Burnt Magnesite for the manufacture of crome magnesite/magnesite-chrome refractories.

TABLE II

Production and export of magnesite

(In Thousand Tonnes)

	1975	1976	1977	1978	1979	1980
1. Production	313.4	329.75	402	414.3	384.7	371
2. Export						
2.1 Raw	—	0.11	3.11	2.41		
2.2 Calcined	9.35	7.29	8.7	4.48	N. A.	N. A.
2.3 Dead Burnt	0.35	0.34	1.28	—		

Refractory Industry shares about 35 per cent of the total consumption of chromite and stands next only to metallurgical needs which consumes about 50 per cent. In India, there is no separate specification for refractory grade chromite. The refractory manufacturers generally accept a chromite with not less than 40 per cent Cr_2O_3 (With total $Cr_2O_3+Al_2O_3$ at least 60 per cent) and not more than 6 per cent SiO_2. Higher Al_2O_3 in chrome ore is desirable. But an important prerequisite is that the ore should be compact, massive, hard and lumpy. Unfortunately, hard and lumpy ores of chromite available in India are generally high in SiO_2 and at some places high in FeO. Although the Indian chromite reserves are reported to be measured 2.32 million tonnes, indicated 6.97 million tonnes and inferred 7.97 million tonnes, that of lumpy refractory grade is about 0.5 million tonnes only. It sounds quite depressing when compared with requirement of chromite for refractory industry which stands at 50–60 thousand tonnes per annum at present and may go up to 90,000 tonnes per annum by 1990.

Orissa is the leading producer of chromite in India and the major producing centres lie in the district of Cuttack, Dhenkanal and Keonjhar. At the same time, the Orissa chromite is also the best grade available in India. Other sources of refractory grade chrome ore are Pauni and Ratnagiri areas of Maharashtra and Hassan district of Karnataka. Refractory grade chromite has also been reported from the Ukhrul district of Manipur.

The proudction, export and internal consumption of chromite for the period from 1975 to 1980 are shown in Table III. It is found that refractory industry in

TABLE III

Production, export and internal consumption of chromite in India

(In Thousand Tonnes)

	1975	1976	1977	1978	1979	1980
1. Production	500.3	402.1	352.2	266.3	309.1	320
2. Export	370.7	277.8	167.1	59.1	N. A.	N. A.
3. Internal consumption						
3.1 Refractory	39.0	44.6	45.9-approxi-mately	50-60		
3.2 Total	84.8	108.6	108.8	N. A.	N. A.	N. A.

India consumes from 30 to 45 per cent of the total internal consumption and production of chromite in India is mainly export oriented.

Dolomite

Dolomite is the source material for the 'Doloma' refractory used for the lining of L. D. furnace. As doloma is cheaper than the conventional magnesia refractory, gradually it is coming into practice in L. D. furnace lining in India. The refractory industry at present consumes around 500,000 tonnes of dolomite annually and the demand in this industry is likely to increase substantially in future.

The dolomite required for L. D. furnace lining has to be of high purity. Particularly the silica content must be less than 3 per cent. At present the supply of refractory grade dolomite is obtained mainly from M. P. partly from Bhutan.

Refractory grade dolomite deposits have been identified in the Jalpaiguri discrict of West Bengal and Bilaspur and Mandla districts of M. P. The estimated reserves in West Bengal and M. P. are 513 and 47 million tonnes respectively.

Future Demand and Outlook

From the estimated requirement of basic refractories in the present decade (Table I) it is found that demand for both chromite and magnesite will increase substantially. Demand for magnesite in 1985 and 1990 are estimated to be of the order of 475,000 and 600,000 tonnes respectively. The same for chromite are estimated to be about 58,000 and 93,000 tonnes respectively. Although projection of demand for dolomite in refractory industry has not yet been made, it is assumed that it will also show the same trend as in case of magnesite and chromite to meet the requirements of the expanding steel industry particularly the plants based on L. D. process. It is more so, as it has been decided to introduce L. D. technology in all the steel plants.

The known reserves of Salem magnesite would not last beyond the present decade, if the same is continuted to be used without any proper planning. Further, insistence to produce a grade having max 2.5 SiO_2 would make the life of the reserve still shorter. The Almora-Pithorgarh and even the addition of Nepal magnesite are not expected to change the situation significantly.

The total reserve of refractory grade hard, lumpychrome ore was estimated towards the end of 1070's to be not more than 0.5 million tonnes. Assuming an average consumption rate of minimum 50,000 tonnes by the refractory industry, no refractory grade chromite will be available towards the late 1980's.

Planned Utilization

It is easily conceivable that the prospect of availabilily of indigeneous raw-materials particularly of magnesite and chromite, for basic refractory is not bright unless a planned utilization is evolved. The refractory industry has been using the best quality raw materials available in every case and this practice has created an impression

of almost complete exhaustion of some type of raw-materials. Beneficiation of low grade ores and search for alternative raw-materials seem to be the two most significant approaches for maintaining continuous flow of required quantity of materials.

Beneficiation

Beneficiation of magnesite, both from Salem and Almora-Pithorgarh deposits has been experimented by NML, Jamshedpur, and Regional Research Laboratories, both at Bhubaneswar and Jorhat.

NML, Jamshedpur is reported to have reduced the silica content of Salem magnesite to a considerable extent by froth flotation and heavy media separation method with about 60 per cent recovery. They report to increase the magnesia content to as high as 90–92 per cent and reduce the silica content to as low as 2 per cent by employing fatty acid flotation method.

RRL, Bhubaneswar has developed a single stage beneficiation technique of Salem magnesite by employing flotation in specially designed flotation column using anionic collector and suitable depressants. By this method it is claimed that the silica could be reduced from 11 to 4.5 per cent i.e. more than 50 per cent of the silica could be removed.

The possibility of beneficiation of off-grade Salem magnesite was studied by RRL, Jorhat by taking advantage of the non-hydraulic nature of silicates formed during light calcination and physico-chemical properties of freshly formed magnesium hydroxide. They reported a method consisting of light calcination, hydration and then separation of hydrated magnesia from the unhydrated contaminents by dispersion in water. A product containing more than 94 per cent MgO, and less than 3 per cent SiO_2 with magnesia recovery of more than 80 per cent was obtained using one off grade magnesite containing 10 per cent SiO_2 as impurities.

However in case of beneficiation of magnesite, not only lowering of the impurities, but maintaining the proper CaO/SiO_2 ratio is also of quite importance, as the silicate phases formed in the matrix of the D.B. magnesite/refractories finally determine the quality of the product. Further beneficiation process will have to be developed according to the nature of impurities. While in case of Salem deposit, it is to be aimed to reduce the SiO_2 content, in case of Almorah-Pithorgarh deposit, it may be necessary to remove the lime and iron content. Moreover, the magnesite which is suitable for ramming mass etc., does not need to be taken up for beneficiation. Similarly the magnesite, as in the case of Salem, which could be upgraded for making high quality refractory, should not be used for fettling etc.

Number of chromite samples have been tested for beneficiation in different laboratories. The ores containing serpentine and talc as gangue minerals could be successfully upgraded by simple gravity methods. In cases where the gangue minerals are present as descrete iron oxide, reduction roast followed by low intensity magnetic separation or flotation are useful. Attempt has also been made for

upgrading off-grade fine chromite, that result during crushing and grinding of relatively soft chromite in refractory plants by simple air separation. Further, in some cases, simple desliming of the material may be enough to obtain a good quality chromite.

As in the case of magnesite, in case of chromite also beneficiation process should be adopted judiciously. The chromite suitable for other industries, like charge chrome which can tolerate higher amount of iron, does not need to be taken up for beneficiation for its utilization in refractory industry. At the same time, the chromite which can not be upgraded to the refractory grade, does not necessarily to be left unprocessed, if it is possible to beneficiate it for utilization in charge-chrome process.

Although laboratory experiments have shown the feasibility of beneficiation of different refractory raw-materials, the processes have not yet been taken up in large-scale beneficiation, partly because of the cost involved and partly because of the problem of using the end product. Beneficiation processes, in most of the cases, need very fine grinding of the materials, while in refractory manufacturing process, it is difficult to accommodate the entire material in the required granulometric composition. Further, pre-calcination of the fine material, wherever it is required is also an additional problem. In view of the above, beneficiation of refractory raw-materials has not yet become popular in India. But in the present condition, it is felt that beneficiation must be adopted to achieve our production and quality target for basic refractories. When beneficiation and subsequent sintering of magnesite have proved to be successful economically and technologically in some other countries, there should not be any apprehension in adopting the same in India. Plants in Austria and Greece beneficiate magnesite by flotation method. USSR adopt heavy media separation. A plant in Yugoslavia uses electrostatic separation for magnesite. Optical sorting has been adopted for separating magnesite from dunitic rock by a plant in Greece. With so much of world-wide adoption of beneficiation processes for low grade magnesite, it is high time now to start beneficiation of low grade magnesite in India on a large scale. It is reported, the RRL, Bhubaneswar has experimented agglomeration of beneficiated fine ahromite. There is also report of adopting the method for commercial utilization. It is emphasized that this method should be widely adopted for utilization of fine chromite in refractory manufacturing process and at the same time, similar technology should be developed even for the other beneficiated fine refractory raw-materials, which require pre-calcination.

Alternative Source

Sea Water Magnesite: Manufacture of magnesia from sea-water on an industrial scale is a well established industry in many countries. High grade extra pure magnesiac an be synthetically prepared from sea water and brine through direct chemical precipitation of insoluble magnesium hydroxide by reacting with lime or dolomite.

The process basically consists of calcining dolomite or limestone and reacting this with sea water, pretreated with H_2SO_4 to remove ca-bicarbonate, to precipitate magnesium hydroxide, which is subsequently dead burnt at a temperature around 1800°C to get the refractory grade magnesia. The product is extra pure and it is possible to get magnesia with as high as 99 per cent MgO. Due to this purity, it is possible to manufacture very high grade refractory bricks. According to the present practice prevailing in India, the requirement of magnesia for the preparation of magnesia bricks for steel making works out to 20 kg per tonne of steel, while experiments have shown that the same prepared from sea water magnesia is only 6 kg per tonne of steel produced. Consequently, the modern steel plants practically all over the world, have switched over to the use of sea water magnesia and at present around 50 per cent of the total world production of magnesia based refractories are manufactured by using sea water magnesia. Today as many as 25 sea water magnesia plants having capacities ranging from 50,000 to 250,000 tpy are in operation in more than 10 countries.

In India, desired quality dolomite and limestone deposits required for the sea water magnesia manufacturing process near to the sea shore have not yet been located. However, this should not be regarded as an obstacle for adopting the process.

Central Salt and Marine chemicals research Institute at Bhavnagar have installed a pilot plant having a production capacity of about 500 kg/day of magnesium hydroxide cake from sea water. The chemical analysis of the product shows MgO 91–95 per cent, CaO up to 2.5 per cent, R_2O_3 up to 2.5 per cent and SiO_2 1.5 to 2.5 per cent.

The major draw-back in the sea water magnesia process is that, as the sea water contains only around 0.13 per cent Mg, to produce one tonne of magnesia it requires approximately 300 tonnes and 600 tonnes of water in dolomite and limestone based process respectively. In this respect, bittern obtained after removing common salt from sea water, which contains around 400 gm $MgCl_2$ per litre may prove to be better source for magnesia. In fact Dalmia Institute of Scientific and Industrial Research, Rajgangpur has developed a process for manufacturing of refractory grade MgO from the bittern as well as from the highly concentrated brine.

(A list of patents is given at the end of the paper.) The Chemical analysis of the product by this process shows MgO up to 98 per cent.

It is highly desirable that the Government of India should come forward to adopt the process of manufacturing magnesia in a pilot plant scale either from sea water or bittern to show its economic viability in India. It seems to be the only answer to the problem relating to stringent demand of high quality basic refractories in the steel industry.

Doloma, Magdol and Magnesia-Carbon

Production of steel by the LD or QBOP process continues to increase worldwide. At present, in Europe, the process accounts for about 75 per cent of total

steel output. India's future plants naturally will have to be based on this practice. The present open hearth furnaces of existing steel plants shall have to be replaced by bottom blown converters as the open hearth process is becoming obsolete. The refractory for a LD converter or a vessel must be capable of resisting attack by basic slags at temperatures at least up to 1700°C and the materials which are readily available for such application are magnesia, doloma and lime. As the reserve of good quality magnesite is very limited, the refractory industry will have to develop proper technology for the utilization of the other two raw materials. Doloma has already come into practice and attempt should be made to perfect the technology, so that maximum replacement of magnesia by low silica dolomite may be possible. Dead burnt limestome has often been suggested as a potential basic refractory. It has been used as refractory in LD vessels in Poland. However, the relative ease with which it hydrates may cause gross production and handling problems. Besides, the lime does not exhibit high resistance to solution in ferritic slags. Another possibility is to blend all these raw-materials in a finely ground state and co-sinter them at high temperature to form a product with the required MgO/CaO content. These are commonly known as magnesia-doloma or magdol clinkers. The large scale production of magdol clinkers is still mostly limited to Japan only. However, with the increasing growth of LD converters naturally one will have to consider the utilization of such newly developed refractory products.

Another magnesia-based refractory, where magnesia can be considerably replaced is magnesia-carbon. Production of magnesia-carbon refractory, with as high as 30 per cent carbon is reported. In this case also, Japan is in the lead. Substitution of magnesia which may be as high as 30 per cent, will definitely ease the situation created by non-availability of quality grade magnesite and keeping this in view, development of magnesia-carbon refractory should be taken up very earnestly by the Indian refractory manufactures.

Fine Chromite

Refractory industry expects the refractory grade chromite to be compact, massive, hard and lumpy, besides having requisite chemical composition. In the process of crushing and grinding, a good amount of fine materials are produced.

In the normal granulometric composition of chromite based refractories, accommodation of all the fine materials is not possible. So, these fine materials get accumulated in the refractory plants. Besides, if the beneficiation of low grade chromite is taken up, this will also produce reasonably high amount of fine materials with suitable chemical composition. The best way to utilize the fine chromite is to fuse or sinter it with magnesite and the resultant products, fused mag-chrome or co-sintered mag-chrome may be used for the production of refractories, with or without addition of extra chromite/magnesite as it may be necessary. The refractories produced by this process are found to be superior to those manufactured by simple firing of chromite with dead burnt magnesite, and the process has become quite common in Western Countries. It is emphasized that in India also, necessary facilities for fusion or at least for sintering of magnesite and

chromite at high temperature should be developed, which will lead to the utilization of otherwise rejected chromite fines for the manufacture of high grade basic refractories.

Some Concluding Observations

With the expansion of the industries particularly that of iron and steel, the requirement of basic refractories is going to increase considerably in the coming decade. Apart from increase in quantity, constantly changing technology in the consumer industries will demand more and more sophisticated refractories. Thus, we foresee a continuously increasing demand for high grade raw materials. Unfortunately India's resources for high grade basic refractories are not adequate. Planned utilization of the available raw meterials is the only answer to the problem relating to sufficient production of high quality basic refractories. In addition to the beneficiation of low grade ores and application of alternate raw materials, the following steps, which are equally applicable to all types of refractory raw-materials, may help in lessening the severity of the problems.

1. The Government should accept immediately the long standing demand of the refractory manufactures for banning the export of all refractory grade raw-materials.
2. Extensive exploration work should be undertaken for all important refractory raw-materials.
3. Mining methods should be improved so that gradewise recovery of raw-materials becomes possible.
4. Practice of utilizing higher grade raw-materials for production of lower grade refractories should be stopped.
5. A concerted effort should be made for proper evaluation and utilization of the available resources.

List of patents on the process for manufacturing

Refractory grade MgO from brine and bittern, obtained by Dalmia Institute of Scientific and Industrial Research : Rajgangpur

Sl. No.	Patent No.	Title	Country
1	2	3	4
1.	151044 dt. 30-4-79	Process for the production of a Solidified Mass containing magnesium compounds rich in magnesium.	India
2.	151045 dt. 30-4-79	Process for preparing of Magnesium Oxide from a Solid mass of Magnesium Chloride.	India
3.	2048843 dt. 9-3-83	Process for the production of magnesium Oxide from Brine or Bittern.	England

Continued

1	2	3	4
4.	4370422 dt. 25-1-83	Process for the production of magnesium oxide from Brine or Bittern.	U.S.A.
5.	225336 dt. 15-3-82	Process for the production of magnesium oxide from Brine or Bittern.	Argentina
6.	1157231 dt. 22-11-83	Process for the production of magnesium oxide from Brine or Bittern.	Canada
7.	195763 dt. 5-12-80	Process for the production magnesium oxide from Brine Bittern.	Newzealand