Beneficiation and utilisation of low grade refractory materials

* N. N. Mathur, * P. C. Sen and * M. R. K. Rao

Introduction :

The present production of refractories in India is of the order of 0.75 million tons. These comprise fireclay, alumino silicates, high alumina and basic refractories and refractory cements, mortars, plastics and castables. Besides these, large tonnages of dead burnt dolomite are produced in many steel plants for fettling and repair of open-hearth and electric arc furnaces or lining L-D vessels. Of the total production of refractories, steel plants consume almost 80%. By and large the refractory manufacturers were coping up with the requirements of user industries except for the demand of some speciality refractories. However with the changing technology, particularly in steel making, and greater emphasis on purity of refractories the refractory manufacturers find it exceedingly difficult to meet the stringent specifications laid down by the users.

Although at present low grade refractory materials are available in huge quantities to last a few more decades, the resources for high grade materials are limited or not upto the required quality.

Further due to ever increasing demand of the industry in terms of quantity and quality of refractory minerals, mechanised mining is adopted. This results in the production of poor quality of R.O.M. ore and a sizeable quantity of fines which go on stock-piling as waste dumps at the mine heads.

In order to make good use of the existing refractory mineral deposits and meet quality specifications it becomes imperative to upgrade the low grade materials as well as the huge quantity of waste materials by suitable beneficiation process.

However, beneficiation has some disadvantage so far as the refractory minerals are concerned. The product of beneficiation is generally a fine material, which generally cannot be used directly in refractory industry unless it is processed to yield a dense, coarse grog acceptable to the refractory manufacturers.

Considerable amount of work has been done in NML on beneficiation of low grade refractory minerals both on bench scale as well as pilot plant scale and industrial flow-sheets have been worked out. A summary of results of some of these studies conducted in the Ore Dressing Division are reported in this paper. Further, attempts are being made in the Refractories Division of NML for utilisation of these beneficiated fines for the production of refractories. Studies are underway to study and establish various process parameters and the economic viability of using such fine materials. Some of these test results have also been included.

Magnesite :

All India production of magnesite in 1981 was around 463000 tonnes of which roughly76% came from Tamilnadu and 21% from U.P. and the rest from Karnataka and Rajasthan. Of the total production of magnesite nearly 63% was consumed by the refractory industry.

The raw material Sub-committee of the Development Panel on Refractories (DGTD) in

* *Scientist,*
National Metallurgical Laboratory,
Jamshedpur-831007.

its interim report had worked out a demand of 590,000 tonnes of magnesite by 1990.

The mineral is mostly used for the production of magnesite and chrome-magnesite bricks. The Indian standard specifications for dead burnt magnesite stipulates 5.5% SiO_2 and 2.5% CaO which means that in the raw state the lime and silica should be about half of these limits. Such low silica and lime magnesites are now scarce. (Table - 1).

In most of the advanced countries very pure quality sea-water magnesia is used for the manufacture of basic bricks for L-D and EAF (Table-2) but in India where this material is not available indigenously resort has to be taken to imports and considerable quantity of sea water magnesia is being imported. Under the circumstances beneficiation of natural magnesites to low SiO_2 and CaO levels is all the more important. Further the beneficiation of the natural magnesite will have the added advantage of low B_2O_3, which is a most deleterious impurity in sea water magnesia. Beneficiation studies on a number of Salem and Almora magnesite samples were conducted at NML. A summary of the results is shown in Table—3.

The chief problem with the two main magnesite deposits of the country, that is Salem and Almora, is the reduction of SiO_2 in the former and CaO in the latter to acceptable limits. Silica and lime occur as finely disseminated inclusions, veins or stringers; any beneficiation process aimed at reducing these impurities necessarily involves fine grinding and flotation is the only suitable method for beneficiation.

Flotation test on Salem magnesite assaying 7.0% SiO_2 showed that the concentrate after three cleanings represented 19.4% of the feed and contained 1.18% SiO_2. But the concentrate after two cleanings assayed 2.21% SiO_2 with a 34.1% yield. A 2.2% SiO_2 magnesite would be a good material for the production of refractories. Studies are under way to evaluate its refractory properties. Preliminary results show that the fines could be utilised to produce a dense grog. Table-4 gives the grain densities of magnesia fired at 1650°C after different agglomeration techniques and Fig. — 1 their microstructures. Pellets gave a sinter of highest density and lowest porosity. It may be mentioned here that grain density of sinter is important as higher densities reduce slag attack and increase service life of refractory.

The Refractories division of N. M. L. has successfully developed a process for the reduction of lime cotent in Almora magnesite by a patented process. The lime content in the dead burnt magnesite could be reduced from 7 % to below 2%, with 85% wt. recovery. The bricks produced from the concentrates meet the required specification.

Kyanite / Sillimanite :

Kyanite and sillimanite are important refractory minerals used for the manufacture of high alumina bricks besides refractory grade bauxites or diaspores. The refractory industry requires bauxites/diaspores of low Fe_2O_3 and TiO_2 contents (Total 3—5% max) and 56—60% Al_2O_3 but such deposits are scarce. Both kyanite and sillimanite have the same chemical composition ($Al_2O_3.SiO_2$) and both transform to mullite on heating but in kyanite this transformation is accompanied by a large volume expansion (16% approx).

Kyanite :

Lapsaburu deposits of Singhbhum district, Bihar which were once the world's best deposits are now getting depleted and the production has been falling. Other known occurences are in Bhandara district in Maharashtra, Chickmagalur, Mandya, Shimoga and South Kanara districts of Karnataka and Udaipur district of Rajasthan. Large reserves of low grade kyanite have been discovered in Khammam and Prakasam districts of Andhra Pradesh, Singhbhum in Bihar and Purulia in West Bengal.

The total reserves of refractory grade kyanite containing 55 % Al_2O_3 (min) are estimated to be 956,000 tonnes of which 90,000 tonnes are under the measured category. The cumulative resource of low grade deposits is placed at over 147 million tonnes.

Sillimanite :

Massive sillimanite occurs in Meghalaya, Maharashtra, Madhya Pradesh and Karnataka. The famous Khasi sillimanite deposit of Meghalaya is diminishing in productivity. Small deposits occur in Tiruchirapalli district of Tamil Nadu. Of recent interest are the secondary sillimanite of Kerala, Tamil Nadu and Orissa beach sands containing 5 — 10 % sillimanite.

The total reserves of sillimanite are of the order of 11.6 million tonnes of which 68,000 tonnes are of massive variety.

The total consumption of kyanite and sillimanite was about 49,200 tonnes in 1981 and the demand by such industries as iron and steel, copper, refractory, cement, lead and zinc and aluminium alone is expected to be 84,600 tonnes by 1990.

Kyanite and sillimanite even in their purest state contain 62.9 % Al_2O_3 and as such cannot be used for the production of high alumina bricks containing more than 60% Al_2O_3. As such the refractory industry needs the purest varieties containing more than 60% Al_2O_3. However for medium range refractory products a 55—60% Al_2O_3 material is adequate. There is therefore a need to beneficiate this second grade kyanite/sillimanite. NML has been seized with the problem and conducted beneficiation studies on a number of kyanite samples. A summary of these tests is given in Table - 5. Studies have also been done towards ultilisation of these fines.

Laboratory scale studies done on a kyanite sample assaying 34.6% Al_2O_3 in R.O.M. gave encouraging results. This sample was beneficiated by flotation and the concentrate which was —72 mesh B.S.S. assayed 60% Al_2O_3. The concentrate was compacted and fired to 1550 and 1650°C. The properties of the fired compacts are shown in Table—6.

It is evident from the table that the concentrated fines can be successfully used for the production of a dense sinter which can subsequently be used for the manufacture of high alumina bricks.

Laboratory scale work has also been done on Kerala beach sands and refractory bricks were made. These bricks compared well with the bricks made from lumpy ores. The properties of bricks are given in Table—7.

Graphite :

Graphite is used for the manufacture of crucibles for melting metals and alloys and stopper heads for teeming ladles. Of late another class of graphite based refractories, containing graphite and refractory oxides like MgO, Al_2O_3 etc. has come up which finds increasing application in steel making furnaces. Some of these applications call for coarse flaky graphite having high resistance to oxidation and low ash content. Indian graphites in general have high ash contents and need beneficiation for such applications.

Flaky crystalline graphite (+65 mesh) is generally used for crucible making and refractory purposes. Natural graphite deposits in India are located in Orissa, Gujarat, Kerala, Tamilnadu, Andhra Pradesh, Rajasthan, Bihar, and Jammu and Kashmir. The estimated total reserve is about 7.8 million tonnes of all grades. Table—8 gives the summary of beneficiation studies on some Indian graphites.

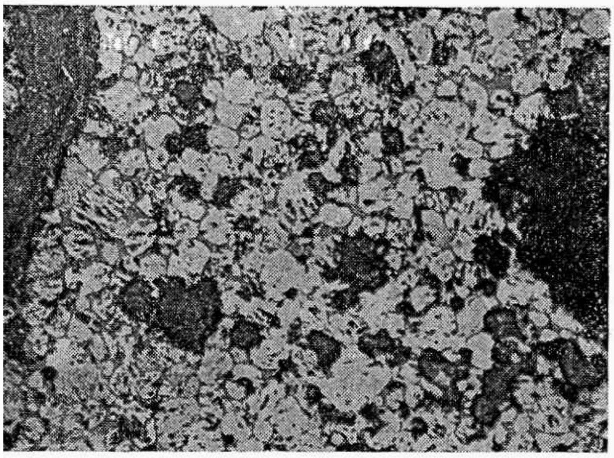
Graphite is used for refractory industry, foundry, lubricant, paint and various other industries for which specification are available. The quality requirement of natural graphite for use in the refractory crucible industries is given in Table—9. The oxidation study of a sample of Kerala graphite beneficiated in the laboratory in comparison with Madagaskar graphite is shown in Table - 10, which showed that the sample is at par with imported flaky graphite. The concentrates were sent for trial production of graphite crucibles at Rajahmundry. They were found to be eminently suitable for crucible manufacture.

Conclusions :

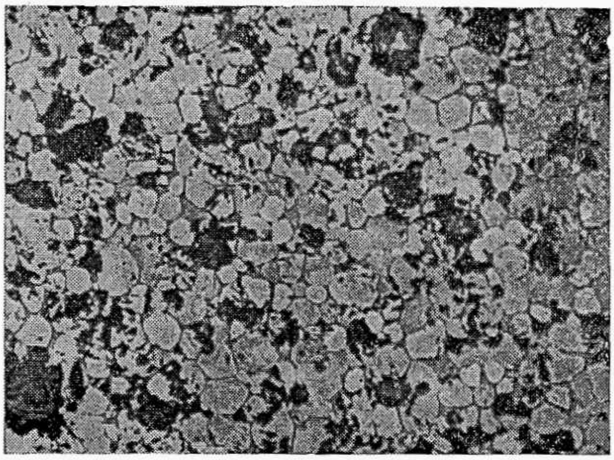
In view of the depleting resources of high grade refractory raw matarials the problem Indian refractory industry is presently confronted with is two-fold. Firstly to get consistent supplies of raw materials such as magnesite, kyanite, sillimanite, graphite etc. conforming to the stringent specifications, leaves no alternative other than beneficiation by suitable methods. Secondly beneficiation would result in the generation of concentrates which are of fine size, usually below 100 mesh. The problem then arises as to its utilisation because this fine material cannot be used as such. Therefore, even if the industry gets the concentrate of requisite quality it will not be able to take up the whole of the concentrate for brick making unless it is suitably processed to yield a dense grog. This requires tailored processes suitable for each concentrate so that it is accepted by the refractory industry for brick making. The technical parameters and economics of such process have to be worked out and work is being done in NML to this end.

Acknowledgement :

The authors are thankful to Prof. V. A. Altekar, Director, National Metallurgical Laboratory for his kind permission to present this paper.



(A)



(B)

Fig. — 1 Microstructure of 1650°C fired brick (A) and pellets (B)

Table — 1 : All India reserves of magnesite as on 1-1-1980 (in tonnes)

State	Measured	Indicated	Inferred	Total
I Reserves of magnesite with Silica upto 3.25%				
Karnataka	—	—	4,500	4,500
Rajasthan	—	23,600	12,000	35,600
Tamil Nadu 1/	—	—	141,224	141,224
Total :	—	23,600	157,724	181,324
II Reserves of magnesite with Silica 0.50% to 10%				
Karnataka	436,000	428,380	134,000	998,380
Kerala	—	15,000	—	15,000
Tamil Nadu 1/	4,638,797	4,635,863	3,369,019	12,643,679
Total :	5,074,797	5,079,243	3,503,019	13,657,059
III Reserves of magnesite with CaO upto 2.5%				
Uttar Pradesh	331,330	7,722,700	20,550,000	28,604,030
IV Reserves of magnesite with CaO 2.5% to 8%				
Uttar Pradesh	4,000,000	11,390,000	2,810,000	18,200,000
V Reserves of magnesite with CaO 0.00% to 9.30%				
Uttar Pradesh	2,451,632	112,465,438	13,716	114,930,786
VI Reserves of magnesite of Unclassified type				
Himachal Pradesh	—	—	87,620	87,620
Rajasthan	—	228,792	—	228,792
Tamil Nadu 1/	1,002,800	93,019	21,644,857	22,740,676
Uttar Pradesh	731,049	941,115	18,071,549	19.743,713
Total :	1,733,849	1,262,926	39,804,026	42,800,801
All India Total :	13,591,608	137,943,907	66,838,485	218,374,000

1/ According to M/s. Dalmia Magnesite Corporation, the insitu inferred reserves in their leasehold are around 20 million tonnes.

Table — 3 : Summary of beneficiation results of some magnesites of Indian origin

Sample State and Locality	R.O.M. Assay% MgO%	R.O.M. Assay% SiO_2%	Beneficiation Method	Concentrate Wt. %	Concentrate Assay% SiO_2
Tamil Nadu					
Salem	44.51	2.85	Heavy Media separation at − 3/4″ + 10 mesh	73.5	1.48
Salem	45.9	3.0	Flotation and cleaning	70.0	0.9
Salem	44.9	1.1	Crushing, sizing at −12 mm + 65 mesh (only screening)	82,0	2.2
Salem	45.86	3.9	Flotation and cleanings	77.6	1.05
Salem (Dead-Burned)	85.7	8.6	Heavy Media Separation/		6.18
			Magnetic separation		7.63
Salem	42.2	7.0	(i) HMS of −25 + 6.33 mm at 2.8	13.2	2.20
			(ii) Flotation (93% −200 mesh) with cleanings	52.4	2.26
			(iii) Flotation with reground midd-ling recirculation	54.8	1.87
Salem	42.2	7.0	Flotation (93% −200 mesh) and Middlings reground (98% −200 mesh and recirculation	53.1	2.30
Karnataka					
Kadakala	38.4	14.7	Flotation and cleanings	48.2	1.73
U. P.					
Pithoragarh (I)	43.65	0.99	CaO Flotation and cleaning with 3.01 Katha for lime removal.	67.8	0.35
Pithoragarh (II)	42.21	1.31	4.04 -Do-		0.70
Rajasthan					
Ajmeer	41.6	9.8	Flotation and cleanings	37.6	1.63

Table — 2 : Chemical Analyses of some magnesites used abroad vis-a-vis Indian magnesites

	Source	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	B_2O_3
Indian :							
Salem	Natural	5.5 — 7.0	1.0 — 1.5	0.5 — 0.1	1.4 — 2.5	89 — 90	—
Almora	Natural	4 — 6	1.0 — 1.5	3.0 — 5.5	17.0	85 — 92	—
Foreign :							
Greece	Natural	0.8	0.20	0.2	1.60	94.87	0.01
Turkey	Natural	1.16	0.04	0.61	2.28	95.88	0.01
Austria	Natural	0.86	0.56	3.91	2.75	91.82	0.08
USSR	Natural	2.4	—	2.6	1.70	92.40	—
Pelletised magnesia							
A	Sea water	0.8	0.4	1.50	1.8	95.5	0.03
B	Sea water	0.8	0.2	0.15	2.0	96.8	0.03
C	Sea water	0.5	0.2	0.15	2.0	97.1	0.04

Table — 4 : Grain density of different compacts made from salem magnesite concentrate and fired at 1650°C

Method of compaction	Grain density, gm/cc
50×50 mm cylindrical specimen	3.30
Bricks (Screw press)	3.27
Pellets	3.37

Table — 7 : Properties of sillimanite bricks made from Kerala Beach sands

Al_2O_3	60 %
SiO_2	36 %
P. C. E.	Cone 38 (Orton), 1850°C
App. Porosity	21—25%
R.U.L.	Ta 1640—1650°C Te 1655—1675°C
C.C.S.	13000—17900 P.S.I.
Thermal spalling (BRRA)	+ 32

Table — 5 : Summary of beneficiation studies on Kyanite

State & Locality	Assay% ROM Al_2O_3	Assay% ROM SiO_2	Yield%	Assay % Conc. Al_2O_3
Andhra Pradesh :				
Khamam	25.4	62.7	21.6	60.0
Bihar :				
Badia	45.3		59.0	60.2
Singhpura	51.2		69.3	61.1
Rajkharswan	54.9		71.7	60.4
Amba-lapso	38.2		30.9	60·4
Sirbali	46.8		45.1	60.1
Lapsa-buru	34.6		22.8	60.0
— do —	35.4		18.4	57.0
Orissa :				
Meganmohan Mines, Pallaharu	51.6		57.1	60.8
Maharashtra :				
Dahagaon Sample - 1	40.1		10.1	57.5
— do — Sample - 2	38.4		27.4	59.6
— do — Sample - 3	49.0		54.4	61.1
Karnataka :				
Mavinkere	64.1		72.5	72.8

Table — 6 : Properties of the sintered compacts of kyanite concentrates.

No.	Sample composition and size				1550°C firing		1650°C firing	
	Kyanite			China clay addition%	Porosity %	B.D. gm/cc	Porosity %	B. D. gm/cc
	−60 mesh	−150 mesh	−300 mesh					
1.	100	—	—	nil	48.6	1.64	46.10	1.74
2.	100	—	—	5	51.6	1.76	34.60	1.97
3.	—	100	—	nil	41.2	1.67	35.09	2.02
4.	—	100	—	5	39.6	1.74	30·35	2.06
5.	—	—	100	nil	32.7	2.06	10.30	2.46
6.	—	—	100	5	33.8	2.06	15.20	2.40

Table—8. Summary of the beneficiation studies on some low grade graphite of Indian origin as done in N. M. L.

Locality	Process	Original analysis	Concentrate analysis	Recovery %
Sitampalli, A. P.	Flotation 55% −200 mesh	17% FC 79% Ash	82% F. C.	91.5
Khepchisbi Hill Bhutan	Flotation	10.66% F. C. 86.4% Ash	63.4% F. C.	78
Palamau, Bihar	Flotation 79.4% −200 mesh	15.5% F. C. 76.5% Ash	88% F. C.	90
Doomara, Ajmer	Flotation −200 mesh	8.19% F. C. 84.37% Ash	Intimately mixed with mica and not amenable to flotation.	
Chammuda Sidhi, M. P.	Flotation	4.86% F. C. 87.34% Ash	Not amenable to beneficiation.	
Panchmahal, Gujrat	Flotation	7.1% F. C. 80% Ash	41.65 F. C.	76.6
Khammam A. P.	Flotation	10.4—64 F. C. 81.7—31.6 Ash	69.5—87.4 F.C.	87—88

Table –9. Specifications of graphite used in crucible industries

	British*	U.S.A.**	India*** (ISI draft)
1. Chemical analysis			
Carbon content	85%	85—90%	90%+
Fe_2O_3			1.2% Max
TiO_2			0.5% Max
CaO			0.02% Max
S			0.5% Max
Volatile			1.5% Max
2. Sieve analysis			
Retained on 8 TSS	—	1%	Particle size between—14 mesh BS to +90 mesh BS
20 ,,	—	8%	
28 ,,	20%	34%	
35 ,,	—	75%	
42 ,,	80%	—	
48 ,,	—	95%	
60 ,,	95%	97%	
Passing 60 ,,	5%	3%	
3. Flakiness index ml/100 gm	129	—	Graphite should be crystalline flaky.
4. Physical requirement	—	—	Graphite should be reasonably free from mica. The oxidation temperature should be approx 750°C

* British crucible makers specification

** National stockpile specification U. S. A. p-22A, 1-14-1947

*** A minimum 80% carbon is acceptable if the balance of impurities is aluminous or sillimanite.

Table—10 : Oxidation loss of two varieties of graphite flakes (−14 +72 B: S. S.)

Temp °C	Madagascar graphite	Kerala State graphite
800	5.5%	6%
900	17%	22%
1000	73%	75%

References :

1. Beneficiation of industrial minerals for the basic refractories. — P. D. Prasada Rao A. Peravadhanulu, N. Chakravorty, S. K. Banerjee and G. P. Mathur. Paper presented at the seminar on basic refractories for Steel making organised by the Indian Ceramic Society, Jamshedpur chapter and National Metallurgical Laboratory on 23—1—1982 and 24—1—1982 at Jamshedpur.

2. NML's experience in the field of mineral beneficiation and conservation. — B. L. Sengupta, G. P. Mathur and V. A. Altekar. Paper presented at "National Mineral Convention" held at New Delhi on 16—18th February, 1981.

3. An appraisal of occurrence and requirements of kyanite in India and a preliminary investigation on the refractory properties and processing of beneficiated kyanite concentrates. — M. R. K. Rao, N. B. Sarkar, P. C. Sen and R. V. Hargave. I. R. No. 914/77 February, 1977.

4. Raw materials for refractories for iron making. — P. C. Sen and M. R. K. Rao. Paper presented at the Seminar on 'Refractories for iron making' organised by the Indian Ceramic Society, Damodar Valley Chapter, at Bokaro on 8th and 9th January, 1983.