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EXTRACTION OF IRON, ALUMINA AND TITANIA FROM ZIARAT LATERITE

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Experiments were conducted on the extraction of iron, alumina and titania from Ziarat laterite by reduction sintering and leaching operations. The effects of the variation of laterite, coke soda and lime were studied using two processes. In two stage process the recoveries of iron and alumina were 88 and 80 respectively whereas in single stage process the recoveries were low. There was, however, no difference in the recovery of titania in the two processes.

Key words: Alumina, Ziarat, Laterite.

INTRODUCTION

In Pakistan the occurrence of laterite together with bauxite is reported from Azad Kashmir, Hyderabad, Sargodha, Rawalpindi, Peshawar and Quetta Division [1, 2]. The Ziarat laterite in Quetta Division is reported to have extensive reserves [3, 4, 5] containing fairly high concentration of alumina, titania and iron oxide. The significant concentration of titanium oxide in the ore makes the ore worth especial consideration.

The work on the geology, age and reserves of Ziarat laterite was conducted by Crookshank and Herron [6], Shah [3], Hunting Survey Corporation Limited [5] and Metzko and Stannin [4]. Detailed geochemistry and mineralogical study was presented by Khan [7]. The preliminary research work on its utilization was conducted by Muhammad [8] Ali and Amin [9] and Shah, Rauf and Mehdi [10]. The present study on the extraction of iron, alumina and titania from the ores mainly deals with reduction sintering of ore with lime and soda followed by leaching operations.

Two procedures for the extraction of iron, alumina and titanium dioxide were studied: (a) two steps method involving iron removal followed by soda lime sintering and leaching the slag for alumina and titanium dioxide recovery [11]; (b) single step reduction and soda lime sintering of the laterite and leaching the slag for alumina and titanium dioxide extraction.

The processes adopted for processing Ziarat laterite are variants of those used for the recovery of iron, alumina and soda from red mud (waste produced from Bayer alumina production from bauxite) [12-16]. The investigation aimed at determining the most suitable composition of the batch and the process for the extraction of iron, alumina and titanium dioxide from Ziarat laterite. The batch composition was made by mixing suitable proportion of lime,

soda and reductant with finely ground laterite. The mixture was agglomerated in a disc pelletizer, dried and weighed in a crucible and reduced in a pot furnace. The contents of the crucible were cooled, dumped on a steel plate and crushed. The reduced iron globules separated by a low-intensity magnetic separator and slag recovered. The products were analysed and the slag was also subjected to X-ray diffraction for phase determination.

The composition of slag was adjusted by varying the amount of lime and soda in the batch, in accordance with the CaO-FeO-SiO₂ phase diagram [17, 18]. As the dissolution of aluminium oxides in alkali depended on the composition of the phase in the slag, the leaching properties of a few slags with regard to the phase transformation during sintering were also studied.

EXPERIMENTAL

Preparation of the raw materials. The bulk samples of the raw materials used in the experiments in the amounts of 50kg laterite ore and 25kg each of coke, marble and quartz, were crushed in a Denver jaw crusher to make a product of approximately 1/2" to 1 1/2" size. This crushed product was then passed through a Denver roll crusher to achieve a material of minus 4 mesh size (BSS).

The roll product was then passed through a disc grinder of 9 1/2" size made by the Mine and Smelter Supply Co., Colorado, to produce a material passing 40 mesh size (BSS). The different ground materials except coke were then fed to a Denver ball mill of 3' x 3' size to prepare a ground material passing 100 mesh BSS. The chemical analyses of laterite, coke and lime stone are reported in Tables 1 and 8.

Experiment on single stage firing. The raw materials were mixed in appropriate proportions, a typical batch composition is given in Table 7.

Table 1. Chemical analysis of average grade of laterite from Akram Tangi (wt. percent).

Al ₂ O ₃	24.14
SiO ₂	3.26
Fe ₂ O ₃	57.10
TiO ₂	4.52
CaO	0.98
MgO	0.20
L.O.I.	9.80
	100.00

Almost all the extraction studies were carried out on the above minerals.

A batch of 5 kg from the mixture was thoroughly moistened with 4 percent water by weight. It was then pelletized in the disc pelletizer and gas fired in a pot furnace using a graphite crucible No. 30 (Diamont Germany). The crucible reached a temperature of approximately 1500° in 3 to 4 hours. The furnace was allowed to cool to room temperature and the cooled mass was broken into pieces. The compact iron ingot was taken out and the rest was crushed to about 4 mesh BSS size in a laboratory hammer mill. The iron globules were picked out by a strong hand magnet. The remaining slag portion was further crushed and ground to pass 100 mesh BSS for leaching studies.

Phase study of the slag. The laterite in this procedure when mixed with lime stone, soda and reductant was quickly smelted. Under suitable conditions, the slag separated from iron contained (Na₂Al₂O₄), (Ca₁₂Al₁₄O₃₃), (β-Ca₂SiO₄), (Ca₂Fe₂O₃) and (CaTiO₃). Leaching the slag with dilute soda solution dissolved alumina. The recovery of Na₂O and Al₂O₃ against CaO content is shown in Fig. 1.

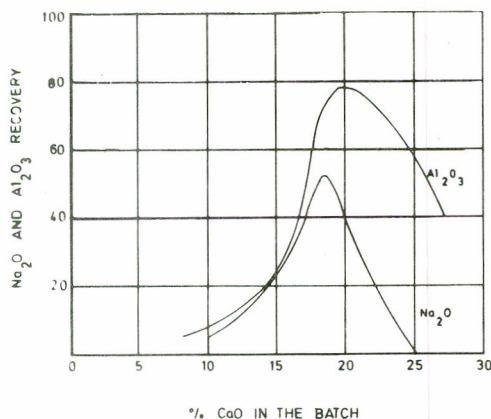


Fig. 1 Effect of CaO addition in the batch.

The steps involved in a single step method employing reduction roasting and smelting were as follows:

- (1) Iron and slag separation.
- (2) Leaching of slag with hot soda solution.

- (3) Leaching of residual mud from step 2 with acid for TiO₂ recovery.

Experiments on two-stage reduction smelting and soda-lime sintering. In the two stage firing soda was substituted by calcium carbonate and fluorite in the first firing step. The steps involved in two stage methods were as follows:

- (1) Reduction of the laterite in a pot furnace and magnetic separation of the reduced iron.
- (2) Sintering the slag obtained from step 1 with soda lime and leaching out aluminium trihydrate.
- (3) Leaching of the residual mud from step 2 with sulphuric acid for titanium dissolution.

The laterite, mixed with a small amount of lime and some reductant was reduced and smelted at about 1460° + 40°. The molten iron and slag were separated. The slag and the lime stone were ground separately in a soda solution and the charge composed had the following molar ratios:

$$\frac{\text{CaO}}{\text{SiO}_2 + 0.5 \text{TiO}_2} = 2.0 \pm 0.05 \text{ and } \frac{\text{Na}_2\text{O}}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} = 0.9 \pm 0.10$$

The slag was sintered in a pot furnace at about 1250°. The sintered mass was wet ground in a rod mill, using hot alkali solution. The pulp was filtered under vacuum. The solution was concentrated and subjected to de-silication. The de-silicated sodium aluminate solution was treated as in standard Bayer process for crystallization to precipitate aluminium trihydrate solution and alkali. The alkali was recycled in the leaching step or recovered.

Titanium dioxide recovery. The grey mud resulting from alumina leaching circuit was leached with concentrated sulphuric acid. The results of the experiments are given in Table 9(a). The leached titanium sulphate was separated from the secondary mud. Iron filings were added in order to reduce Fe³⁺ to Fe²⁺ stage. The clear solution was hydrolysed to precipitate Ti(OH)₄. This was filtered dried and calcined to produce TiO₂.

RESULTS AND DISCUSSION

Effect of lime addition on the phase transformation in two stage process. For the purpose of getting vitreous slag from the laterite, it was considered expedient to change the CaO content in the batch. This was achieved using 8-25 percent lime stone during smelting. About 0.75 part C to 1.0 part of iron present in the batch was used. The composition of some typical slag compositions is given in Table 2.

The iron was separated by magnetic separation from the slags. The average composition of iron is given in Table 3. The iron recovered has to be adjusted with respect to Si

Table 2. Effect of lime addition on the composition of slag.

Test No.	Al ₂ O ₃	SiO ₂	FeO	TiO ₂	CaO	MgO
TS 07	51.00	28.8	4.2	9.1	5.6	1.3
TS 08	49.4	27.4	3.95	8.15	10.21	0.90
TS 09	46.0	25.8	3.62	7.38	16.35	0.84
TS 10	44.7	24.3	3.12	7.06	19.94	0.81
TS 11	41.3	22.5	3.05	6.95	25.44	0.77

Table 3. Chemical analysis of iron recovered during smelting of the laterite (wt. percent).

Fe	92.3
Si	0.26
Ti	0.34
P	0.05
S	0.01
C	3.80
Iron recovery	88.4

Table 4. Chemical analysis of sinter and mud.

Compound	Sinter	Mud
Al ₂ O ₃	24.40	6.53
SiO ₂	13.80	24.10
Fe ₂ O ₃	2.24	3.92
TiO ₂	4.34	7.74
CaO	28.60	50.85
MgO	0.61	1.10
Na ₂ O	26.00	4.90
L.O.I.	—	1.12

The overall yield of Al₂O₃ extraction on the basis of alumina content in laterite was found to be about 85%.

Table 5. Chemical analysis of secondary mud (after titanium extraction).

Al ₂ O ₃	2.42
SiO ₂	26.55
Fe ₂ O ₃	4.13
TiO ₂	0.75
CaO	53.70
MgO	1.83
SO ₃	6.25
L.O.I.	4.18

Table 8. Analysis of coke and limestone (wt. percent).

	Fixed carbon	Volatile matter	Ash	P	S	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	L.O.I
Coke	86.0	0.92	12.34	0.04	0.62	5.94	5.00	2.60	0.53	0.16	—
Limestone	—	—	—	—	0.01	5.43	0.62	0.88	50.20	1.12	38.9

and Mn, in order to make it foundry grade. The iron could be converted into steel.

The X-ray diffraction studies of the slag samples (listed in Table 2), showed that on increasing CaO content, carnegitite was formed beside nephylene. In the slag TS 09, perowskite (CaO, TiO₂) was also present alongwith Na₆Al₄Si₄O₁₇ crystalline phase. On further addition of lime in sample No. TS 10, gehlenite (2CaO.Al₂O₃.SiO₂) was also determined. At high CaO content nephylene phase almost disappeared, whereas the amount of perowskite and vitreous phase remained constant. At higher CaO content, however, as in sample TS 11, the glass phase was low, besides, the slag became very viscous.

Sintering the slag. The slag from the reduction smelting step was sintered with soda using sodium carbonate. The sinter was leached with dilute soda solution at tem-

Table 6. Chemical composition of slag and mud in single step process.

Compound	Slag	Mud
Al ₂ O ₃	30.4	10.8
SiO ₂	4.6	8.3
Fe ₂ O ₃	4.5	8.1
TiO ₂	6.6	9.4
CaO	40.5	50.6
MgO	40.2	0.4
Na ₂ O	12.2	2.1
L.O.I.	—	10.3

Table 7. Technical data on the single stage sintering – leaching of laterite.

Raw materials		
Laterite kg		1,000
Coke kg		0,750
Limestone kg		0,170
Soda kg		0,150
Recoveries per tonne of laterite		
Constituents	kg/t	Percent recovery
Iron	327	88
Al ₂ O ₃	146	59
TiO ₂	40	90

peratures 60-90°. A typical composition of sinter and the mud, resulted from leaching the sodium aluminate is given in Table 4. The effect of variation of coke, lime and soda on the recovery is shown in Table 11. The overall yield of Al_2O_3 extraction on the basis of alumina content in laterite was found to be about 80%.

Titanium oxide extraction. The mud obtained was leached with concentrated sulphuric acid, in an agitated

cell. The $CaO.TiO_2$ phase formed during sintering process was decomposed into $Ti(SO_4)_2$. Some iron present as FeO was also leached. On standing some of the $FeSO_4$ was converted into $Fe_2(SO_4)_3$. This phase with time lapse precipitated to $Fe_2O_3.H_2O$. The situation was avoided by reducing Fe^{+++} to Fe^{++} with metallic iron. The mud was filtered, the clear solution was hydrolysed with alkali in order to precipitate $Ti(OH)_4$. The precipitate was filtered, dried and cal-

Table 9. Leaching of titanium dioxide from the alumina leach residue.

Sr. No.	Nature of the material	Strength of H_2SO_4 v/v (%)	Vol. of the acid (mls.)	Wt. of the material per 100 ml acid (g)	Temperature of leaching ($^{\circ}C$)	Time of leaching (hrs.)	Recovery of TiO_2 (%)	Normality of the acid in 200 ml leach solution	Acid consumed calculated ml. of conc. H_2SO_4	Wt. of Fe^{++} leached per g (mg)	Wt. of Fe^{+++} leached per g (mg)	Wt. of total iron leached per g (mg)
1.	Washed leach residue	40	100	8	Boiling	2	92.40	5.8 N	7.8	-	-	-
2.	"	40	80	10	100	1	99.3	4.4 N	7.4	-	-	-
3.	"	40	80	10	100	1/2	99.6	3.0 N	15.2	-	-	-
4.	"	40	80	10	80-85	2	95.7	4.0 N	9.8	-	-	-
5.	"	40	80	10	80-85	1	94.3	3.1 N	15.0	-	-	-
6.	"	40	80	10	80-85	1/2	95.06	3.2 N	14.2	29.8	-	-
7.	"	40	80	10	100	2	97.36	2.7 N	16.8	9.4	-	-
8.	"	40	80	10	100	1	90.39	2.8 N	16.2	9.6	Nil	9.6
9.	"	40	80	10	100	1/2	86.62	2.8 N	16.4	8.8	0.5	9.3
10.	"	40	80	10	80-85	1	91.49	2.8 N	16.6	8.8	0.6	9.4
11.	"	40	80	10	80-85	2	97.89	2.9 N	16.0	10.7	-	-
12.	"	40	80	10	R.T.(30)	1/2	14.58	3.1 N	16.0	20.3	11.2	31.5
13.	"	40	80	10	R.T.(30)	1	93.33	3.1 N	14.9	21.7	8.8	30.5
14.	Leach residue of slag 57	40	100	8	Boiling	2	94.99	-	-	-	-	-

Table 9(a). Leaching of titanium dioxide from the slags prior to Al_2O_3 leaching.

Sr. No.	Nature of the material	Strength of H_2SO_4 (%) v/v	Vol. of the acid (mls.)	Wt. of the material per 100 ml acid (gms)	Temperature of leaching ($^{\circ}C$)	Time of leaching (hrs.)	Recovery of TiO_2 (%)	Normality of the acid in 200 ml leach solution	Acid consumed calculated as mls. of H_2SO_4
1.	Leached residue (semi leached)	30	85	12	90	1	42.4	-	-
2.	"	23	125	8	90	1	62.9	3.06 N	12
3.	"	30	125	8	90	1	68.07	5.1 N	9.9
4.	"	30	70	14	90	1	58.59	2.38 N	8.2
5.	"	30	85	12	90	1	62.18	3.0 N	9.3
6.	"	40	125	8	90	1	69.8	-	-
7.	"	40	100	8	100	1	76.2	-	-
8.	Slag 57	40	100	10	100	1	89.5	-	-
9.	Slag 53	40	100	10	100	1	69.6	-	-
10.	Leach residue of slag 57	40	100	8	Boiling	2	95.0	-	-

Table 10. Leaching of alumina from the slag.

Sr. No.	Mode of slag formation	Strength of NaOH solution g/100 ml	Volume of the leach solution (ml)	Weight of the slag per 100 ml solution (gm)	Temperature of leaching (°C)	Time of leaching (min)	Recovery of Al ₂ O ₃ (%)
1.	Single stage process	10	100	5	70 ± 5	60	42.73
2.	"	15	100	5	70 ± 5	60	58.4
3.	"	20	100	5	70 ± 5	60	56.17
4.	"	25	100	5	70 ± 5	60	67.06
5.	"	15	100	5	50 ± 5	60	34.61
6.	"	15	100	5	60 ± 5	60	65.3
7.	"	15	100	5	80 ± 5	60	52.4
8.	"	15	100	5	90 ± 5	60	61.6
9.	"	15	100	5	70 ± 5	20	47.65
10.	"	15	100	5	70 ± 5	40	62.71
11.	"	15	100	5	70 ± 5	90	74.88
12.	Two stage process	10	100	10	70 ± 5	60	67.45
13.	"	15	100	10	70 ± 5	60	85.23
14.	"	20	100	10	70 ± 5	60	87.54
15.	"	25	100	10	70 ± 5	60	91.67
16.	"	15	100	10	50 ± 5	60	51.85
17.	"	15	100	10	60 ± 5	60	90.63
18.	"	15	100	10	80 ± 5	60	70.37
19.	"	15	100	10	90 ± 5	60	77.94
20.	"	15	100	10	70 ± 5	20	60.72
21.	"	15	100	10	70 ± 5	40	82.35
22.	"	15	100	10	70 ± 5	90	90.27

Table 11. Effect of varying amounts of coke, lime and soda on the recovery of iron, alumina and titania using 750 kg coke/1000 kg laterite.

Sr. No.	Weight of lime and soda per 100 kg laterite		Percentage recovery of Al ₂ O ₃ *		Remarks
	Limestone kg	Soda ash kg	Two steps process	Single step process	
1.	150	150	68	48	Excessive use of lime increases the loss of soda during smelting in the single step process. Excessive use of soda results in no further increase in recovery.
2.	170	150	80	60	
3.	190	150	63	42	
4.	170	130	45	33	
5.	170	140	58	40	
6.	170	160	80	60	

The recovery of TiO₂ varies little in the experiments.

cined. The composition of the secondary mud is given in the Table 5.

The recovery of TiO₂ on the ore basis corresponded to over 80 percent. The product however, contained some Al₂O₃, which needed separation in a separate purification step.

Technical data on two steps process. Technical data on the extraction of iron, alumina and titanium dioxide from Ziarat laterite are as follows:

Alumina recover

Laterite	kg/t Al ₂ O ₃	3,850
Coke	kg/t Al ₂ O ₃	460
Soda	kg/t Al ₂ O ₃	60

Titanium recover

Laterite	kg/t TiO ₂	20,000
Sulphuric acid	kg/t TiO ₂	2,250

Iron recovery

Laterite	kg/t iron	3,400
Coke	kg/t iron	750
Lime stone	kg/t iron	96

Single stage process. Bench tests have shown that iron and Al_2O_3 contents of the laterite could be obtained in one stage process. The laterite was mixed with lime and soda, the mixture was reduced and then smelted in a crucible. The slag was cooled slowly in order to achieve self dusting material of the composition $CaO.Al_2O_3$ and $12 CaO.7Al_2O_3$. In cases where the slag was cooled quickly or quenched in water, vitreous phases of composition $3CaO.Al_2O_3$ and $CaO.2Al_2O_3$ also appeared, which are least leachable compounds. The composition of the slag and mud after leaching is given in Table 6.

It was observed that loss of Na_2O during reduction was from 5-20 percent. During smelting, however, especially in the presence of increasing proportion of CaO , the loss of Na_2O was recovered as high as 50 percent. The smelting time therefore should be decreased in order to reduce the loss of soda. The slag produced in this process was rather vitreous. The leaching period for vitreous slag had to be extended from 2-10 hours. For amorphous slags, on the other hand, Al_2O_3 leaching over 60 percent was achieved in 1-2 hours.

The single stage leaching process although appeared procedurally attractive and energy saving, yet, the alumina recovery was lower in comparison to the two stage process, Table 10. Also, there was greater loss of soda in single stage reduction sintering. The overall recoveries per tonne of laterite and the raw materials consumption are given in Table 7.

CONCLUSIONS

There was no difference in the recovery of titanium dioxide in single stage or two stage process for the processing of laterite.

The extraction and recovery of alumina, however, differed in the two approaches:

1. Iron, alumina and titania were extracted from the complex treatment of laterite using single stage process. The recovery of alumina was however, low in the case of single stage method. Also, at higher temperature of smelting higher loss of Na_2O was observed.

2. In two stage process on the other hand the recovery of iron (85 percent metallized) was over 88 percent. The slag on leaching yielding over 80 per cent aluminium oxide recovery. The resulting grey mud after the alumina recovery was leached with acid to dissolve out titanium values to the extent of 90 percent. On the basis of Bench scale tests, it was calculated that 1 tonne of the laterite would yield 260 kg Al_2O_3 , 290 kg iron (85% metallization) and 50 kg TiO_2 . In single stage process the recoveries of Al_2O_3 were rather low. Besides, the loss of Na_2O was high.

There is a need for more systematic work on the development of single stage extraction process in order to improve the efficiency.

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