ALUMINOTHERMIC REDUCTION OF ANATASE CONCENTRATES

LINO R. FREITAS*, Metallurgical Engineer, M.Sc. and Ph.D.

PAULO R. MAZONI*, Metallurgical Engineer

MAGID W. SAAB*, Metallurgical Engineer, M.Sc.

* Center of Technology, Companhia Vale do Rio Doce,
Belo Horizonte-MG, Brazil

ABSTRACT

The aluminothermic reduction of anatase concentrates (80-86% TiO_2), from Tapira-MG, Brazil, has been studied in an open, alumina-lined reactor.

Thermodynamic calculations, as well as the preliminary experiments, indicated that the reaction is not sufficiently exothermic to enable separation of the products. Therefore, additional heat is necessary and a heat booster such as sodium chlorate ($NaClO_3$) was employed. It was found that $NaClO_3$ additions in excess of 15% of the TiO_2 content in the feed charge were required to obtain good metal/slag separation.

Batch tests with a maximum charge of 15 kg of concentrate were performed and titanium recoveries up to 74% were obtained. The effect of the following variables on the titanium yield was determined: amount of feed charge, amount of fluxes (lime and fluorspar), particle size of reagents and amount of aluminium in excess of the stoichiometric quantity.

Additional tests with Australian rutile and synthetic titanium dioxide as feed materials were performed, with similar results. Also, experiments without boosters, but with external heating were conducted and comparable titanium recoveries were obtained.

INTRODUCTION

The aluminothermic reduction, also known as the thermite process, is widely used in the preparation of ferro-alloys. Presently, Fe-W, Fe-Mo, Fe-Nb and Fe-Ti, among others, are being produced aluminothermically in a commercial scale[1].

Recently, considerable efforts have been made to develop the aluminothermic reduction route for the production of some refractory metals. In this way, the preparation of vanadium, tantalum, niobium and molybednum from the pure oxides has been the subject of several papers [2-5]. In these studies, the crude reduced metal was later submitted to a refining step, such as electron beam melting or molten salt electrolysis. The literature on the production of titanium by aluminothermic reduction, however, is very limited and is concerned mainly with pure TiO_2 or rutile [6,7].

In the work presented here, anatase concentrates from Brazil have been used as a raw material for the aluminothermic process. Initially, some thermodynamic aspects of the process were studied, with an emphasis on the establishment of a heat balance. Later, work was done to select the optimum operating conditions. For comparison, experiments were also undertaken using concentrated Australian rutile and pure TiO_2. Finally, tests were carried out using external heating to enhance the aluminothermic process.

THERMODYNAMIC ASPECTS

General

The aluminothermic reduction can be expressed by the following reaction, where M represents the metal of interest:

$$MO_2 + 4/3\ Al = M + 2/3\ Al_2O_3$$

Ideally, the heat evolved by this reaction is sufficient to produce molten, low viscosity metal and slag for a period long enough to allow the denser metal to separate from the slag and to sink to the bottom of the melt.

Several means of enhancing the aluminothermic reduction can be employed. If the heat of reaction is insufficient to produce good metal-slag separation, thermal boosters such as KNO_3, $NaNO_3$, $KClO_3$ or $NaClO_3$ can be used. The reaction of these substances with aluminium is sufficiently exothermic to compensate for the heat defficiency of the system. In addition, the melting point of the alumina reaction product may be decreased by the use of fluxes, lime and fluorspar being the most commonly employed.

Heat Balance

The main objective of the heat balance presented in this section is to estimate the maximum temperature (T_{MAX}) achieved by a system containing anatase ore, aluminium, sodium chlorate and lime. Naturally, this estimation of T_{MAX} has some limitations, which are decribed below:

- the anatase ore is far more complex than a simple mixture of the oxide components
- there is lack of thermodynamic data for

the heat of formation of the alloy and the slag
- the difficulties of establishing the heat losses

In performing the calculations, the following assumptions have been made, some of which from data obtained in our preliminary experiments:

- a fixed excess of 10 wt% of the aluminium necessary for both the reduction of the concentrate and for the reaction with sodium chlorate is used
- the concentrate is assumed to contain 85% TiO_2 and 7.5% Fe_2O_3. The alloy and slag compositions obtained depend upon the amount of lime and sodium chlorate used
- 70% of the TiO_2 in the concentrate is reduced to Ti; the remainder is reduced to TiO, entering the slag
- 75% of the iron oxide is reduced to Fe; the remaining Fe_2O_3 is contained in the slag
- any lime added combines with alumina to form the compound $CaO.2Al_2O_3$, which remains in the slag.

The reactions considered are:

$$3\ TiO_2 + 4\ Al = 3\ Ti + 2\ Al_2O_3 \qquad (1)$$

$$3\ TiO_2 + 2\ Al = 3\ TiO + Al_2O_3 \qquad (2)$$

$$Fe_2O_3 + 2\ Al = 2\ Fe + Al_2O_3 \qquad (3)$$

$$CaO + 2\ Al_2O_3 = CaO.2Al_2O_3 \qquad (4)$$

$$NaClO_3 + 2\ Al = NaCl + Al_2O_3 \qquad (5)$$

Thermodynamic data for reactions (1) to (4), as well as heat capacities for all substances, have been taken from the work of Kelley[8]. The enthalpy change for reaction (5) was obtained from Perfect[9].

Calculations are schematically presented in Table 1.

TABLE 1 - HEAT BALANCE FOR THE ALUMINOTHERMIC REDUCTION OF ANATASE

INPUT	OUTPUT
E_1 = heat of the reduction reactions	S_1 = heat content of the alloy
E_2 = heat of formation of the slag	S_2 = heat content of the slag
E_3 = heat of formation of the alloy	S_3 = heat content of gaseous NaCl
E_4 = heat of reaction with $NaClO_3$	S_4 = heat losses

Since E_3 is expected to be small and no data are available, its value has been neglected. As for the heat losses, they were assumed to account for 30% of the heat input ($S_4 = 0.3\Sigma E_i$). Setting input = output, after some algebric manipulation, an equation of the type is derived,

$$\beta T^3_{MAX} + \delta T^2_{MAX} - \alpha T_{MAX} + \gamma = 0$$

where the parameters α, β, γ and δ depend on the amounts of lime and sodium chlorate used and T_{MAX} is the maximum temperature achieved during reduction. This equation can be numerically solved for T_{MAX} and results for fixed amounts of CaO and $NaClO_3$ are summarized in Table 2. The parameter $\%NaClO_3$ represents the ratio $NaClO_3/TiO_2$ in the feed charge, while %CaO is the ratio CaO/total aluminium charged. Taking into account the results from Table 2 and considering the range 1700-1800°C for the melting point of the slag[10] - which contains 60-70 wt% Al_2O_3, from mass balance calculations - as the temperature constraint for metal-slag separation, it can be seen that additions of $NaClO_3$ in excess of 15% are necessary to enable recovery of the products. Lime additions lower somewhat the values of T_{MAX}, acting in this case as a diluent.

TABLE 2 - MAXIMUM TEMPERATURE (^{o}C) FOR THE ALUMINOTHERMIC REDUCTION OF ANATASE

$\%NaClO_3$ / %CaO	10	15	20	25	30	35
0	1552	1776	1978	2161	2329	2482
10	1520	1739	1937	2116	2281	2431
20	1490	1704	1897	2073	2234	2382
30	1460	1670	1860	2032	2190	2334
40	1432	1638	1824	1993	2147	2289

EXPERIMENTAL

Different anatase concentrate samples were supplied by CVRD concentration pilot-plant in Tapira-MG, Brazil. In most experiments, fine intermediate concentrates were used and their chemical composition is indicated in Table 3.

The atomized aluminium powders tested were commercial grades (99.8% Al), supplied by ALCOA, Brazil and differed primarily in particle size distribution. Comparisons were made on the basis of the mean particle diameter, calculated from screen analysis provided by ALCOA. Other reagents such as sodium chlorate ($NaClO_3$), lime (CaO) and fluorspar (CaF_2), obtained from local suppliers, were of technical grade.

TABLE 3 - CHEMICAL COMPOSITION OF ANATASE CONCENTRATES

COMPOUND	TiO_2	Fe_2O_3	P_2O_5	Al_2O_3	SiO_2	RE_2O_3*	Nb_2O_5
WT%	83.0-86.5	5.0-7.5	2.0-2.5	1.5-2.5	1.0-1.5	1.0-2.0	0.5-0.8

* RE = rare earth oxides, mainly Ce and La

For the open reductions, a mild steel reactor, 110 cm high, 45 cm diameter, lined with high-alumina bricks was employed. In each test, the reactor was placed on the top of a lined circular pit, which was previously prepared in a slag bed, made of slag from previous tests - see Figure 1.

The reactants were mixed intimately in a V-shaped rotating mixer for 20 minutes and charged into the lined reactor. A typical charge is as follows:

Anatase concentrate:	8.0 kg
Aluminium powder:	4.6 kg
Sodium chlorate:	2.3 kg
Calcined lime:	1.4 kg
Fluorspar:	0.7 kg

The aluminothermic reduction was initiated by pouring a few drops of glycerin onto a small amount of potassium permanganate placed on top of the charge surface. Soon afterwards the main spontaneous reaction got started, lasting for about 1-2 minutes. Immediatly after the reaction was completed, the reactor was lifted, allowing the molten slag to flow over the slag bed. The resulting titanium-rich alloy is collected beneath a thin layer of slag, after several hours of cooling to room temperature.

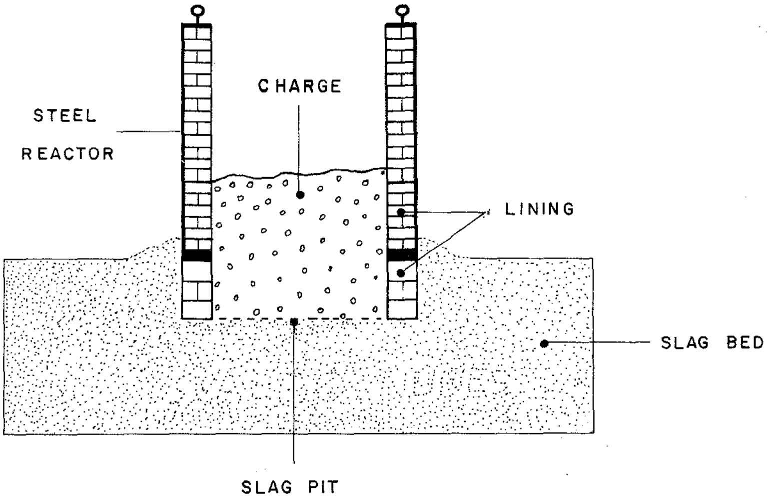

FIGURE 1 - OPEN ALUMINOTHERMIC EQUIPMENT

Tests in which external heating was used were conducted in a RUHSTRAT, type HTR-32, electrical furnace, 60 KVA, 3 phase, with graphite resistors, capable of achieving up to 3000°C. In each test, the furnace was heated to about 1200°C, under argon atmosphere. The argon flow was then stopped and the reaction charge carefully introduced inside a 30 cm high, 7 cm OD, high-magnesia crucible, kept inside the reaction chamber. The reaction charge consisted of approximately 400g mixed reactants - ore, aluminium powder and fluxes - held inside a thin aluminium foil. Once the argon flow was resumed, the furnace temperature was rapidly increased above 1800°C, and kept at this level for at least half an hour. It was observed that tne thermite reaction was initiated when the charge temperature reached about 700°C. Reaction products were collected after several hours of cooling to room temperature, again under argon flow.

OPEN REDUCTIONS WITH ANATASE ORE

As stated previously, the aluminothermic reduction of anatase concentrates yields a titanium-rich alloy and a slag, which contains a mixture of aluminium, calcium and lower titanium oxides. The composition range of the products obtained is indicated in Table 4.

X-ray diffraction analysis on the Ti-rich alloy samples indicated the presence of the following metallic phases, in variable proportions: $AlTi_2$, $AlTi_3$, Ti and Fe_2Ti. In addition, Al_2O_3 was also identified in metallic samples, indicating that a major part of the Al contained in the alloy is actually present as Al_2O_3. The main phases identified in slag samples were $CaO.2Al_2O_3$, $3CaO.5Al_2O_3$ and Al_2O_3. It is noteworthy that TiO_2 was only detected in slag samples after prolonged heating to 1000°C, further confirming that titanium is present in the slag as amourphous titanium sub-oxides.

TABLE 4 - COMPOSITION RANGE OF THE REACTION PRODUCTS (WT%)

METAL	SLAG
Ti: 57.0-72.0	Al_2O_3 : 51.0-65.0
Al: 5.5-20.0	CaO : 6.0-20.0
Fe: 5.5-20.0	TiO : 7.0-20.0
Si: 1.0- 3.0	Fe_2O_3 : 1.0- 3.5
P : 0.7- 2.3	SiO_2 : 0.5- 2.0
Nb: 0.7- 1.2	CeO_2 : 0.35-0.45
	La_2O_3 : 0.20-0.45

An extensive series of reduction experiments was undertaken, holding all parameters but one constant. Variables included charge size, lime, sodium chlorate and fluorspar quantity, amount of aluminium in excess of the stoichiometric quantity and particle size of reagents.

The titanium recovery is calculated as follows:

$$R_{Ti}(\%) = \left[\text{(alloy weight) (Ti cont.in alloy)} / \text{(Ti content in charge)} \right] \times 100$$

This recovery was found to be dependent on the volume occupied by the reaction charge inside the aluminothermic furnace. This is indicated in Figure 2, which shows results of a series of experiments using variable amounts of concentrate in the charge, keeping the same proportions of Al, CaO, $NaClO_3$ and CaF_2. It was observed that the maximum titanium yield was obtained with a charge of 16.6 kg, containing 8 kg of anatase. From this charge, approximately 3.9 kg of alloy were recovered and in subsequent tests the same amount of concentrate was employed.

With small charges, the heat losses are high, due to the great surface area to volume ratio of the charge. With bigger charges, however, the amount of material expelled from the furnace becomes significant, causing the recovery again to decrease.

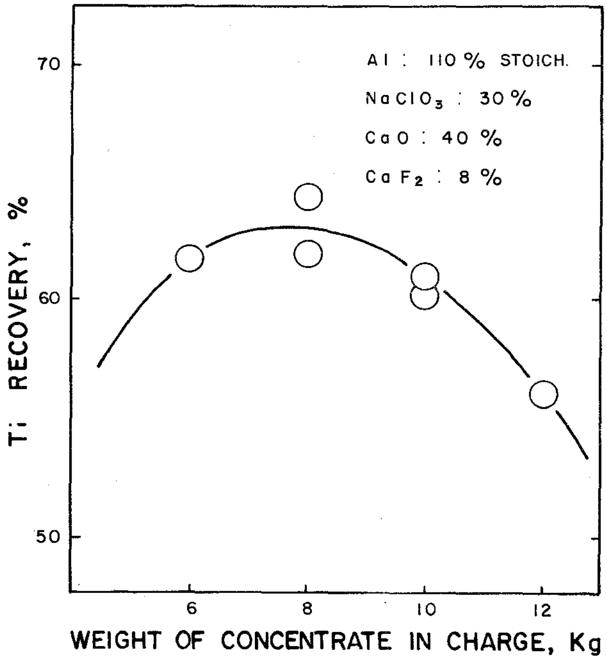

FIGURE 2 - TITANIUM RECOVERY AS A FUNCTION OF THE WEIGHT OF CONCENTRATE IN THE CHARGE

Figures 3 and 4 show the influence of lime and fluorspar additions on the titanium recovery. The behaviour of both fluxes is similar, since an optimum range of addition was found to occur. As stated before, fluxes improve metal-slag separation by reducing the melting point of the slag and thus usually the viscosity at a given temperature. High amount of fluxes, however, lower the maximum temperature reached by the system, since some of the heat generated during reduction must be used to raise both CaO and CaF_2 temperature, which in turn provokes a decrease in recovery.

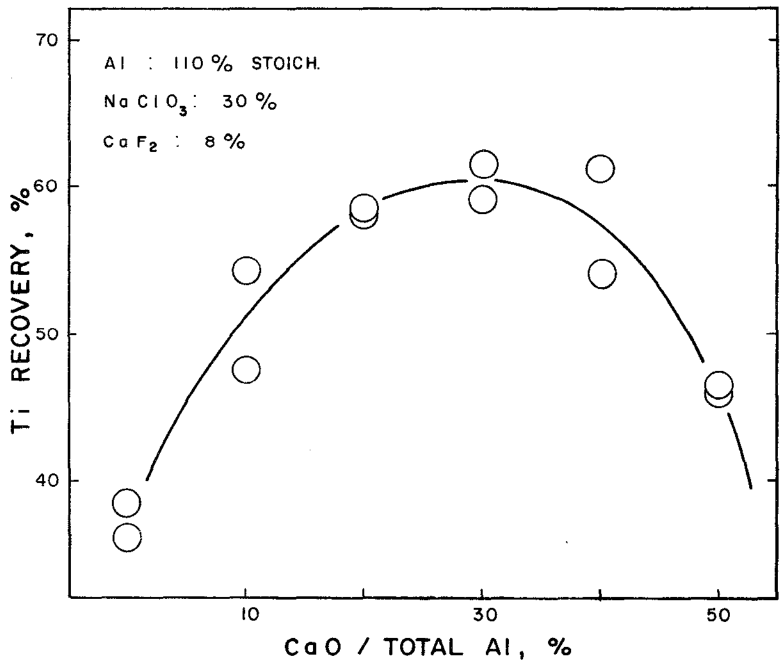

FIGURE 3 - TITANIUM RECOVERY AS A FUNCTION OF LIME ADDITIONS

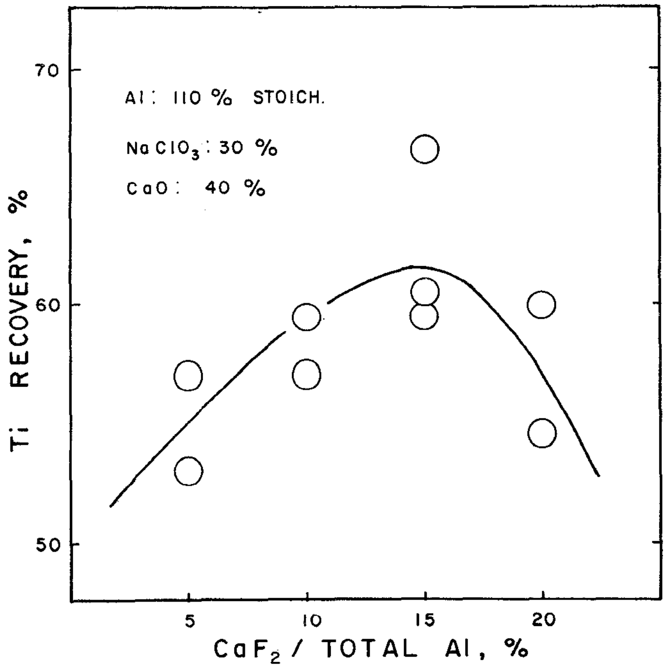

FIGURE 4 - TITANIUM RECOVERY AS A FUNCTION OF FLUORSPAR ADDITIONS

Preliminary experiments showed that no metal-slag separation occurs with sodium chlorate additions below 15% of the total TiO_2 in the reaction charge, confirming the results from the heat balance previously presented. Within the 20-35% range, a maximum titanium recovery was observed using 25% $NaClO_3$, as indicated in Figure 5. This result can be explained on the basis of the following arguments. With low $NaClO_3$ additions, the amount of heat generated during reduction is insufficient to enable separation of the products. On the other hand, when too much $NaClO_3$ is present, the reaction is very violent,with intense agitation of the molten products, with a consequent hindering effect on alloy recovery.

The effect of the amount of aluminium in the reaction charge is indicated in Figure 6. It can be seen that yields increase linearly with aluminium additions, although some scater in the data occured. This result was expected, as an excess of reductant shifts the equilibrium of the aluminothermic reaction towards the products size, thus increasing the recovery. The Al content in the alloy product, however, also increases, reaching about 20 wt% when the amount of aluminium employed is 50% in excess of the stoichiometric, as shown in Figure 7. Since aluminium is a very expensive reagent, the choice of the reductant quantity will represent a compromise between the additional titanium recovery and the consequent aluminium impurification of the final product. We estimate that a 10% excess of aluminium over the stoichiometric, yielding an alloy containing 8-10% Al is probably the best choice. This amount was adopted in subsequent tests.

The titanium recovery was also found to be dependent on particle size of reagents, as indicated in the data of Figure 8. In these experiments, the particle size of the anatase concentrate and aluminium was simultaneously varied in the 44-210µ range, while other additives ($NaClO_3$, CaO and CaF_2) were used as received. Figure 8 also presents results from a series of tests (indicated by the Δ symbol), in which the mean particle size of the anatase concentrate was 9µ, corresponding to results previously presented - see Figure 6. In these tests, the aluminium powder fineness was 44µ, which is the minimum available size of the Al powder-ALCOA no. 101. As particle size varies, there is a maximum yield near 68% at the 40-60µ range. Thereafter, increases in both Al and concentrate granulometry cause the recovery to progressively fall below 60%. There was some evidence that this drop in recovery was not straight, but rather cyclic, more experiments being needed, however, to precisely establish the shape of the curve. For the tests in which finer ore was used, the big difference between Al and concentrate size can be accounted for the low recoveries observed.

In a final series of experiments, the reactor case was left in place overnight, after the reduction, so that the products could cool slowly and freeze. In this series, using the experimental conditions which provided maximum yields (Figures 2-8), 4.0-4.3 kg of alloys containing 70-72% Ti were collected, corresponding to a titanium recovery of 70-74%, which represents a major improvement in the process.

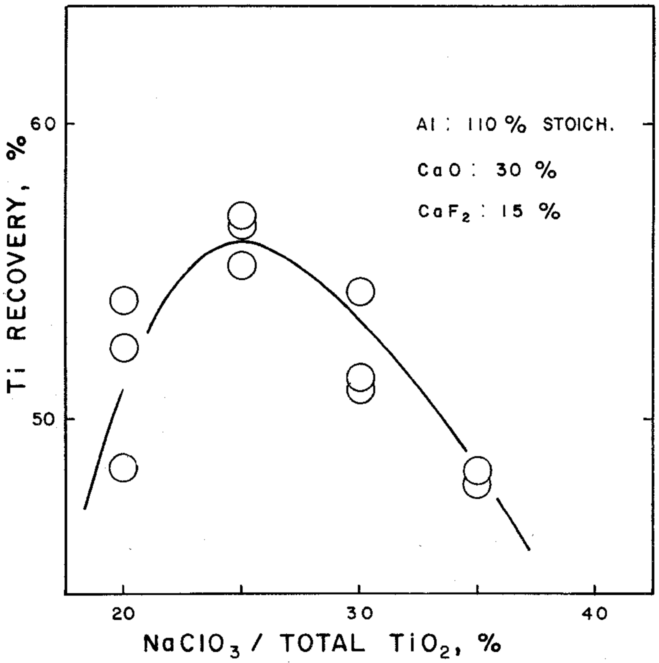

FIGURE 5 - TITANIUM RECOVERY AS A FUNCTION OF SODIUM CHLORATE ADDITIONS

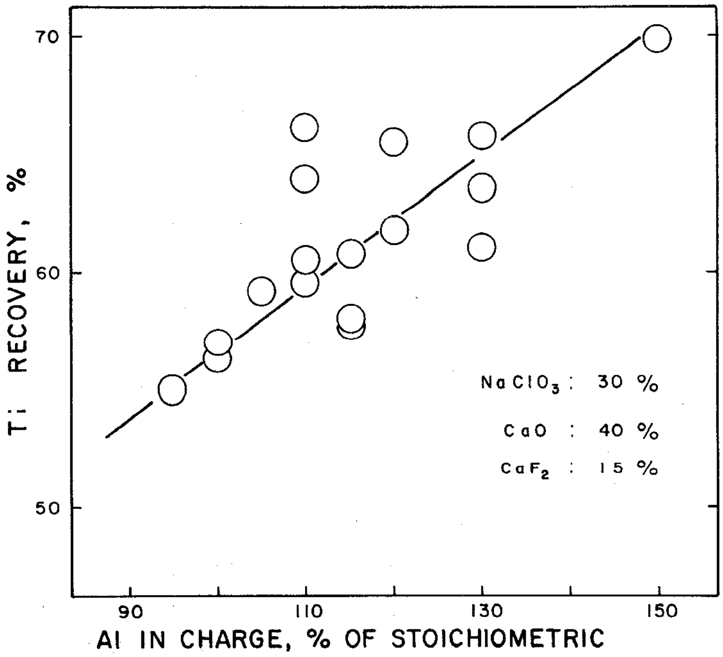

FIGURE 6 - EFFECT OF ALUMINIUM QUANTITY IN THE CHARGE ON THE TITANIUM RECOVERY

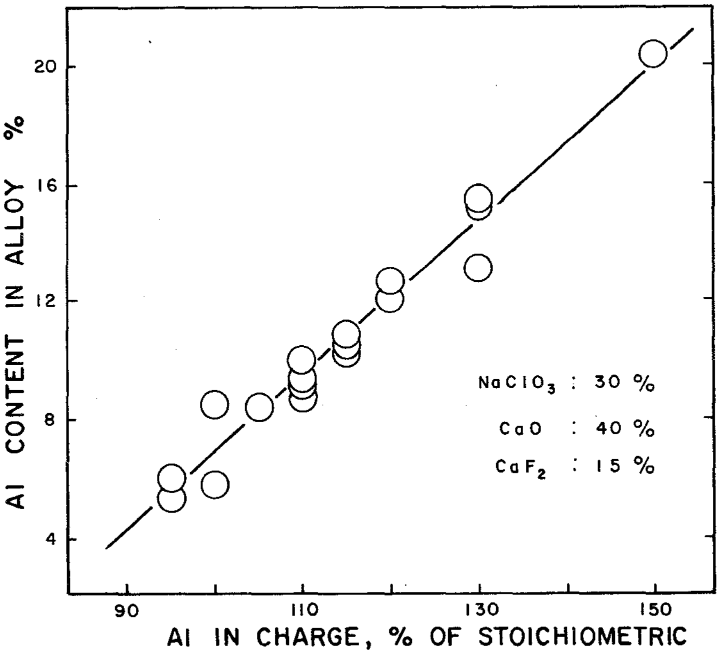

FIGURE 7 - EFFECT OF ALUMINIUM QUANTITY IN THE CHARGE ON THE Al CONTENT OF THE ALLOY PRODUCT

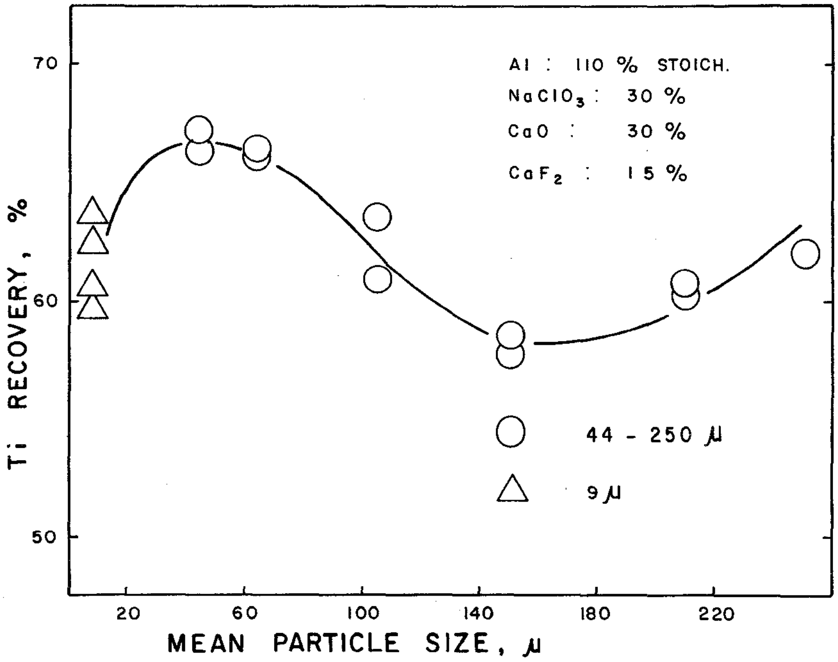

FIGURE 8 - EFFECT OF PARTICLE SIZE OF REAGENTS ON THE TITANIUM RECOVERY

ADDITIONAL TESTS

During the open reduction program, some important questions related to technical and economical aspects of the aluminothermic process arose. These questions have provoked the realization of extra tests, with the following objectives:

- to evaluate if the process is applicable to other titanium-containing materials
- to lower both aluminium and sodium chlorate consumption, thus decreasing the Al content in the final alloy.

Tests With Other Materials

Results of tests in which other titanium-containing materials were employed are summarized in Table 5. Aluminium, sodium chlorate, lime and fluorspar were used in the same proportions as in previous experiments.

It is well known that anatase transforms into rutile on heating [11], and therefore it was felt worthwhile to perform a test with anatase concentrate which had been heated overnight to 1200°C and ground. Results from Table 5 indicate that yields with anatase, both natural or synthetic, were substantially higher than with rutile. This suggests that anatase is more suitable for the aluminothermic process, even though rutile can be used as a feed material if necessary. No further work was done on this topic.

TABLE 5 - ALUMINOTHERMIC REDUCTION WITH OTHER TITANIUM-CONTAINING MATERIALS

RAW MATERIAL	WEIGHT OF CONCENTRATE IN CHARGE (kg)	WEIGHT OF ALLOY (Kg)	Ti RECOVERY (%)
TiO_2 pigment (anatase) (≃ 96% TiO_2)	8.3	4.8 (71.1% Ti)	71.5
Australian rutile (98% TiO_2)	10.0	3.7 (68.4% Ti)	43.1
Rutilized anatase* (79% TiO_2)	11.9	4.6 (65.5% Ti)	53.5

* anatase concentrate heated overnight to 1200°C

Tests With External Heating

In the earlier experiments, the heat defficiency of the system TiO_2-Al was compensated by the addition of a 30% excess aluminium and its stoichiometric equivalent of sodium chlorate. Because of the high cost of these reagents and the associated mass of residue produced, alternative methods of heating were sought.

Table 6 shows results of the tests in which electrical heating was applied. It can be seen that titanium yields were a disappointing 50%, possibly because the experimental conditions were sub-optimum. The final material balance was not exact, because the high-magnesia crucible cracked as a result of thermal shocks during the test, which in turn caused the molten reaction products to leak out into the furnace. These tests will, however be continued using more appropriate techniques, as it is felt that there is considerable scope for improvement.

TABLE 6 - ALUMINOTHERMIC REDUCTION UNDER EXTERNAL HEATING

RAW MATERIAL	WEIGHT OF CONCENTRATE IN CHARGE (g)	WEIGHT OF ALLOY (g)	Ti RECOVERY (%)
Anatase concentrate (83.6% TiO_2)	250	92 (67.9% Ti)	49.9
TiO_2 pigment (anatase) ($\simeq 96\%$ TiO_2)	165	78 (69.4% Ti)	54.8
TiO_2 pigment (anatase) ($\simeq 96\%$ TiO_2)	160	66 (70.2% Ti)	50.3

CONCLUSIONS

1) With the use of the aluminothermic process to the reduction of Brazilian anatase concentrates, it is possible to produce an alloy containing 70% Ti, approximately, with titanium recoveries as high as 74%. Results using rutile as a starting material indicated recoveries of about 50%, only.

2) To make the reaction proceed efficiently, it was necessary to employ an extra heat supply, produced either chemically or electrically.

3) The optimum conditions using $NaClO_3$ as a chemical source of heat were:
   - concentrate + Al size: 40-60µ
   - aluminium: 10% over stoichiometric
   - $NaClO_3$: 25% of the TiO_2 content
   - CaO: 30% the total aluminium
   - CaF_2: 15% of the total aluminium

4) The use of electrical heating was only briefly investigated, but showed sufficient promise for new experiments to be carried out in this way.

5) The product alloy has potential as a source of pure titanium metal or as a direct additive in the preparation of certain alloyed steels, provided the contaminants (P, S...) level meet specifications.

6) The product slag can be a potencial source for recovering the rare earths initially contained in the anatase concentrate.

ACKNOWLEDGEMENTS

The authors are indebted to Companhia Vale do Rio Doce for permission to publish this work. Thanks are also due to Messrs. A. Fonseca and J. Correa, whose dedication in conducting part of the experiments is greatly appreciated.

REFERENCES

1) D.Belitskus, "Aluminothermic Production of Ferro-Alloys", *Journal of Metals*, 25(5)(1973)pp. 39-44.

2) M.B.Mourão and J.D.T.Capocchi, "Estudo Experimental da Aluminotermia do Pentóxido de Vanádio", *Metalurgia-ABM*, 39(306)(1983)pp. 261-265.

3) K.U.Nair, T.K.Mukherjee and C.K.Gupta, "Production of Tantalum Metal by the Aluminothermic Reduction of Tantalum Pentoxide", *Journal of the Less-Common Metals*, 41(1975)pp. 87-95.

4) H.A.Wilhelm, F.A.Schimidt and T.G.Ellis, "Columbium Metal by the Aluminothermic Reduction of Cb_2O_5", *Journal of Metals*, 18(12)(1966)pp. 1303-1308.

5) T.K.Mukherjee, D.K.Bose and C.K.Gupta, "Studies on Molybdenum Extraction", pp. 19-31 in *Extractive Metallurgy of Refractory Metals*;AIME, New York, 1981.

6) J.M.Merle, "Process for Chemically Purifying and Refining Metals", U.S. Patent no. 2,395,286 (1946).

7) C.M.Olson, "Titanium Metal Production", U.S. Patent no. 2,917,440 (1959).

8) K.K.Kelley, "Contributions to the Data on Theoretical Metallurgy, vol. XII", Bulletin 584, U.S. Governement Printing Office, Washington, 1960.

9) F.H.Perfect, "Metalothermic Reduction of Oxides in Water-Cooled Copper Furnaces", *Transactions AIME*, 239(1967)pp. 1282-1286.

10) H.M.Pielet and D.Bhattacharya, "Thermodynamic of Nozzle Blockage in Continuous Casting of Calcium-Containing Steels", *Metallurgical Transactions*, 15B(1984)pp. 547-562.

11) *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 23, pp. 139-140, John Wiley and Sons, New York, 1983.