MOLTEN SALT CHLORINATION OF A BRAZILIAN TITANIUM ORE

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ABSTRACT

In the frame of the beneficiation program of an anatase titanium ore, a carbo-chlorination process of very fine particles of high TiO₂ content (80%) in molten NaCl at 880°C has been developed at a kilogram pilot scale. Titanium tetrachloride, 99% pure, has been obtained with yields as high as 98% and a mean velocity of 1000 mol.m⁻²h⁻¹. Mass balance-sheets, performed on melt, residue and gas samples, have demonstrated the following facts:
- the stoichiometry is two C and two Cl₂ for one Ti,
- the alkaline-earth and rare-earth impurities contained in the ore are completely chlorinated (>99%) and dissolve in the melt enabling a subsequent recuperation.

INTRODUCTION

Anatase, an allotropic variety of rutile, can be found in "Minas Gerais" state in the center of Brazil under the form of huge and high TiO₂ content deposits (reserves over 10⁹t with a 25% average content), and are being beneficiated by the top brazilian mining company "CVRD", through a wide program called "Projeto Titanio".

In the present phase, this program is mainly aimed toward a 4x10⁵t/y production of a 90% TiO₂ concentrate for the chlorine route pigment industries. An original up-grading process has been developed by CVRD (1) in order to take into account the specificity of this world unique titanium ore deposit, and a 15000 t/y pilot plant has been running for 3 years producing a concentrate with the characteristics collected in table 1-A. In this process, quantities, as high as 4 times the production, are evolved as sub-product under the form of fine particles (>400 mesh) of high titanium oxide content, as shown in table 1-B.
These particles, which are much too small to be used in the fluidized bed chlorine process for pigment production (2), are, on the contrary, an excellent material for reactions in molten salt media due to the high specific surface of exchange (3,4).

The work presented here describes the batch production of titanium tetrachloride at a kilogram pilot scale by chlorination of these anatase fine particles, and the subsequent recuperation of rare-earth impurities of much higher financial interest.

CHOICE OF PARAMETERS

Though chlorination of titanium oxide ores be widely described (5), few processes have been developed in molten salts (6 to 17) and none for the anatase variety. Consequently, parameters such as temperature, medium and chlorinating agent have been chosen as undermentioned.

-Temperature : for kinetics reasons, most of reactions described in molten salts have been undertaken at temperatures higher than 700°C, even with lower melting point melts, as it has been shown that below this temperature the rate of reaction drops sharply (11,18).

-Melt : for the above mentioned kinetics reasons, as well as for economical ones, molten sodium chloride has been used as solvent at a temperature ranging 10° around 880°C.

-Chlorinating agent : as shown in table 2, chlorination by Cl₂ or by HCl is thermodynamically impossible for the major part of the oxides present in the anatase concentrate at 1150K (19). At this temperature, the most efficient chlorinating mixture, carbon and chlorine, has been used, the former being obtained from charcoal in-situ decomposition during the heating step of the whole charge. In fact, thermogravimetric studies have shown that carbon is obtained with a yield of 90%, while 9 to 9.5% volatile compounds are expelled around 300°C, the balance being obtained with ashes.

-Granulometry : though this parameter be settled at less than 400 mesh by the fabrication process, attempts to evaluate its influence on kinetics have been made by sintering fine particles up to 3 mesh and chlorinating them respectively.

EQUIPMENT

The pilot unit is composed by four main parts, such as heating device, reactor, condensation set, and scrubbing device, as represented in fig.1.

-The heating device is a 13 kw furnace composed by two hemi-cylindrical parts separable by moving them along a rail track. It is thermostatically regulated in three different regions.
The reactor is a silica vessel, 2.8m high and 0.1m in diameter, composed of a jacket thermoregulated top, a central body in which is introduced a tube with a porous silica disk, and a bottom containing a crucible for collecting the molten salt after operation. The whole set is operated as in the pictogram represented in fig. 2.

The condensation set is composed of two vessels. The first one, filled with NaCl, is maintained at 200°C in order to trap NbCl₅ and FeCl₃ in the form of liquid chloride complex. The second vessel is cooled down in order to condense the evolved titanium tetrachloride.

The destruction of excess chlorine is obtained by scrubbing outlet gases with a concentrated soda shower, recirculated from a 1001. tank.

RESULTS AND DISCUSSION

The function analysis of the whole process is as represented in fig. 3 and gave the following results:

-Chlorination proceeds according to the reaction

\[ \text{TiO}_2 + 2 \text{Cl}_2 + 2 \text{C} = \text{TiCl}_4 + 2 \text{CO} \]

as the mean values of C/Ti and Cl₂/Ti ratios for 12 runs at 880°C have been found equal to 2.0 with an uncertainty of 0.1 respectively. This result is in agreement with previous works in the same temperature range (4,9).

-The maximum chlorination yield for titanium di-oxide has been found around 98% at 880°C, which is in good agreement with the results of Balkova in molten carnalite at 900°C (6), and significantly higher than in a classical process (2).

-The rate of chlorination was found respectively equal to \(10^4\), \(1.3\times10^3\), \(7.5\times10^2\), and \(4\times10^2\)mol.m⁻²h⁻¹, for 400, 32, 9, and 3 mesh feed material granulometry. These values are higher than those available in literature, probably thanks to anatase high reactivity and low granulometry. For example, Sultanova and col.(16) obtained rates in the range 3 to \(6\times10^{-2}\) mol.m⁻²h⁻¹ at temperatures around 700°C in molten carnalite. Another result, claimed in a Japanese patent(9), is \(0.25\) mol.h⁻¹ for a 0.45 kg NaCl melt at 900°C, which, assuming a reasonable cylindrical shape, would correspond to a rate of about \(100\) mol.m⁻²h⁻¹. A velocity of \(0.13\) mol.h⁻¹ is given in the example of a French chlorination patent(17) in a 10 kg reactor, which, with the same assumptions as above, would lead to a chlorination rate of \(20\) mol.m⁻²h⁻¹, a value that can be explained by the low temperature used (470°C) and the granulometry (100 mesh).

-The chemical analysis of TiCl₄ obtained for two different yields are reported in table 3 and demonstrate that the purity is over 99%, while the one obtained by the fluidized bed process is around 98.5% (20,21). This can be explained by a trapping and filtering effect of the molten salt bath.
The impurities contained in the feed material (see table 1) are chlorinated more or less according to the order of $\Delta G$ indicated in table 2. Non-volatile ones, such as alkaline-earth and rare-earth, are completely dissolved in the melt, as shown in table 4. Their recuperation under the form of chloride compounds is possible by reversing the chlorine flow and filtering the melt through the porous silica disk.

CONCLUSION

The set of results obtained on a dozen runs of this pilot unit demonstrated the feasibility of production of high-grade titanium tetrachloride by molten salt chlorination. The advantages of this process with respect to the fluidized-bed one are, on one side, the use of a sub-product that is too fine and too rich in compounds which give clogging non-volatile chlorides, and on the other side, the purity of the obtained product and the possible recuperation of high-value rare-earth compounds.

For these reasons, a prototype plant of 1000 t/y capacity is to be built at CVRD's for early 1988, by "Extramet", a French company specialized in molten salts process engineering.

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Table 1: Chemical analysis of concentrated anatase ore (1-A) and anatase fines (1-B), in weight percent.

| Oxide     | Concentrate A | Fines B |
|-----------|---------------|---------|
| TiO₂      | 89.20         | 82.01   |
| Fe₂O₃     | 4.80          | 3.77    |
| Al₂O₃     | 1.40          | 2.33    |
| SiO₂      | 3.50          | 0.83    |
| P₂O₅      | 1.22          | 3.66    |
| Nb₂O₅     | 0.56          | 0.78    |
| CaO       | 0.20          | 0.85    |
| BaO       | 0.10          | 0.15    |
| MgO       | 0.10          | 0.07    |
| CeO₂      | 0.39          | 1.45    |
| La₂O₃     | 0.16          | 0.92    |
| Y₂O₃      | 0.01          | 0.09    |

Table 2: Free energy values (kcal/mol) for chlorination reactions at 1150 K, according to (19).

| Oxide | TiO₂ | Fe₂O₃ | Al₂O₃ | SiO₂ | P₂O₅ | CaO  | BaO  | MgO  |
|-------|------|-------|-------|------|------|------|------|------|
| ΔG for Cl₂ | 24.38 | 17.70 | 66.17 | 47.44 | 55.29 | -29.30 | -56.51 | 2.46 |
| ΔG for HCl  | 31.57 | 28.49 | 76.96 | 54.63 | 66.07 | -25.71 | -52.90 | 6.05 |
| ΔG for Cl₂/C | -75.61 | -132.2 | -83.82 | -52.51 | -94.60 | -79.32 | -106.50 | -47.52 |
Table 3: TiCl$_4$ chemical analysis (weight %) for anatase fines chlorination yields of 97.5 and 70.0 % respectively.

| Chlorination yield | 97.5 | 70.0 |
|--------------------|------|------|
| TiCl$_4$           | 99.39| 99.32|
| FeCl$_3$           | 0.08 | 0.04 |
| AlCl$_3$           | 0.18 | 0.28 |
| SiCl$_4$           | 0.07 | 0.05 |
| POCl$_3$           | 0.01 | 0.04 |
| NbCl$_5$           | 0.05 | 0.05 |
| CaCl$_2$           | 0.02 | 0.01 |
| BaCl$_2$           | 0.02 | 0.02 |
| MgCl$_2$           | 0.01 | 0.008|
| CeCl$_3$           | 0.15 | 0.15 |
| LaCl$_3$           | 0.02 | 0.02 |
| YCl$_3$            | 0.008| 0.006|

Table 4: Chlorination yields and mass percentages of remaining elements in the melt at 880°C.

| Element | Ti | Fe | Al | Si | P | Nb | Ca | Ba | Mg | Ce | La | C |
|---------|----|----|----|----|---|----|----|----|----|----|----|---|
| Chlorination yield | 97.5 | 99.5 | 86.5 | 79.0 | 89.0 | 96.5 | 99.5 | 99.5 | 96.0 | 99.5 | 99.9 | 94.0 |
| % in melt | 6.0 | 33.0 | 74.5 | 95.0 | 39.0 | 6.5 | 100 | 100 | 100 | 90.0 | 99.2 | - |
Figure 1: Pilot unit for batch kilogram scale chlorination of anatase in molten salt.
Figure 2: Procedure pictogram for the chlorination of anatase in molten salt.
Figure 3: Function analysis of the chlorination process of anatase in molten salt.