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Titania slag smelting and calcination of crude zinc oxide: examples of processing under thermodynamic and kinetic constraints

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Abstract

The main feedstock used for the production of titanium dioxide pigment and titanium metal is natural ilmenite (containing 50% or more TiO₂). However, some ironmaking processes, such as blast furnace ironmaking at Panzhihua and electric furnace ironmaking at New Zealand Steel and Highveld Steel, produce substantial volumes of slag with more than 20% TiO₂. The impurities in such slags cannot be removed by smelting; ilmenite smelting can only eliminate iron oxide. This contrasts with the Waelz kiln processes, which recovers zinc by volatilisation. Dust carried over with the zinc fume affect subsequent calcination, by causing partial melting which impedes movement of the calcine through the calcination kiln.

Introduction

While the principle of obtaining value from slags and dusts is appealing, the individual and combined behaviour of the complex assemblage of compounds in slags and/or in dusts need to be considered when designing and operating a process to extract value. This paper discusses two rather different examples, as a way to illustrate this principle. The first deals with possible processing of TiO₂-rich slags to obtain TiO₂ feedstocks; in the case of smelting, upgrading is by subtraction of impurities rather than by specific extraction of titanium compounds, and this is effective only for removal of iron oxide – so high-quality feedstocks cannot be produced from feed that contains any more than trace levels of impurity oxides (which are essentially anything other than titanium or iron oxides). The second example deals with recovery of zinc from electric furnace dust which, in contrast, allows for targeted removal of zinc as vapour, and its capture as solid zinc oxide. Purification of the zinc oxide is affected by trace impurities that transfer with the zinc vapour. The common theme to these two examples is that it is essential to understand the behaviour of not only the major element(s) or compound(s) to be recovered, but also that of accompanying impurities.

Limitations to titanium feedstock upgrading by smelting

Ilmenite smelting overview

The principles of ilmenite smelting have been reviewed recently,¹ so only a brief summary is given here. The purpose of ilmenite smelting is to yield slag which is suitable for fluidised-bed chlorination, which produces TiCl_4 which can be used to produce TiO_2 pigment (and, to a much smaller extent, titanium metal).² The feedstock is ilmenite (nominally FeTiO_3 in composition, but also containing small percentages of MnO , SiO_2 , Al_2O_3 , CaO and MgO as the main impurities). The ilmenite is fed into an electrical furnace with a high-purity carbonaceous reductant. Partial reduction occurs, removing FeO from the slag to form a metallic iron bath, and leaving behind TiO_2 -enriched slag with a typical titanium content of 85% if expressed as TiO_2 . (In reality up to half the titanium in the slag is in trivalent form; the rest is mainly tetravalent). The typical process temperature – controlled by the presence of a slag freeze lining and hence dependent on the slag melting point³ – is in the range of 1600-1700°C. While this is a reduction process, conditions in the furnace are not highly reducing; around 10% FeO remains in the slag, resulting in an oxygen activity in the slag⁴ of $\log(p_{\text{O}_2}/\text{atm}) \sim -11$. This is not much more reducing than in oxygen steelmaking, which is normally regarded as a relatively oxidising process, with $\log(p_{\text{O}_2}/\text{atm}) \sim -9$. In comparison, the oxygen activity in the hearth of a blast furnace – assuming equilibrium between carbon-saturated iron and a gas in which $p_{\text{CO}} = 1 \text{ atm}$ at 1500°C – is $\log(p_{\text{O}_2}/\text{atm}) \sim -16$.

As a direct result of the mildly reducing conditions, only FeO is reduced to any significant extent from the slag, and all other oxides remain unaffected. Ilmenite smelting is a process that is designed to remove only iron oxide; given the high purity of many natural ilmenites, this is sufficient to yield high-titanium slag which meets the purity requirements of subsequent chlorination. Typical compositional requirements for chlorinatable slag are listed in Table 1.

Table 1: Typical composition of titanium slag for TiCl_4 production by chlorination (wt%)¹

Ti_{tot} as TiO_2	Ti_2O_3	FeO	SiO_2	Al_2O_3	CaO	MgO	MnO	Cr_2O_3	V_2O_5
> 85	< 35	< 12	< 2	< 1.5	< 0.13	< 1.2	< 2	< 0.25	< 0.6

The purity requirements are met by careful selection and beneficiation of the raw materials – ilmenite and reductant – and avoiding contamination from refractory. Where high-purity ilmenite is not available, the slag product cannot be chlorinated,

or it is upgraded by additional oxidative roasting and leaching, to be made suitable for chlorination.⁵

TiO₂-containing by-product slags

Several plants around the world produce iron from titanium-containing magnetite. Examples are in Panzhihua (China) (blast furnace),⁶ New Zealand Steel (electrical furnace),⁷ and Highveld Steel (South Africa) (electrical furnace).⁸ The titanium content of the resulting slags (expressed as TiO₂) is more than 20%, and can exceed 32%. However, these slags are very different from ilmenite, in containing high levels of oxides other than TiO_x and FeO. For example, the New Zealand Steel slag was reported to contain 18% SiO₂, 13% MgO, 16% CaO, 17% Al₂O₃ and 1% MnO.⁷ The resulting complex structure of solidified slag is illustrated in Figure 1.

Unlike ilmenite, these complex slags cannot be upgraded by smelting (since none of the major impurity oxides in the slags is reducible under ilmenite smelting conditions). Because of the propensity of titanium to form compounds and solid solutions, complex processing is needed to recover titanium oxide from such slags. An example is oxidation of molten Panzhihua slag to promote precipitation of perovskite (CaTiO₃), which can subsequently be recovered from solidified slag by grinding and flotation.⁶ It has been shown that the perovskite can subsequently be upgraded to TiO₂ by alkali roasting and acid leaching,⁹ or the previously developed phosphate glass process may be applicable.¹⁰ For Highveld Steel slag, a sulphuric

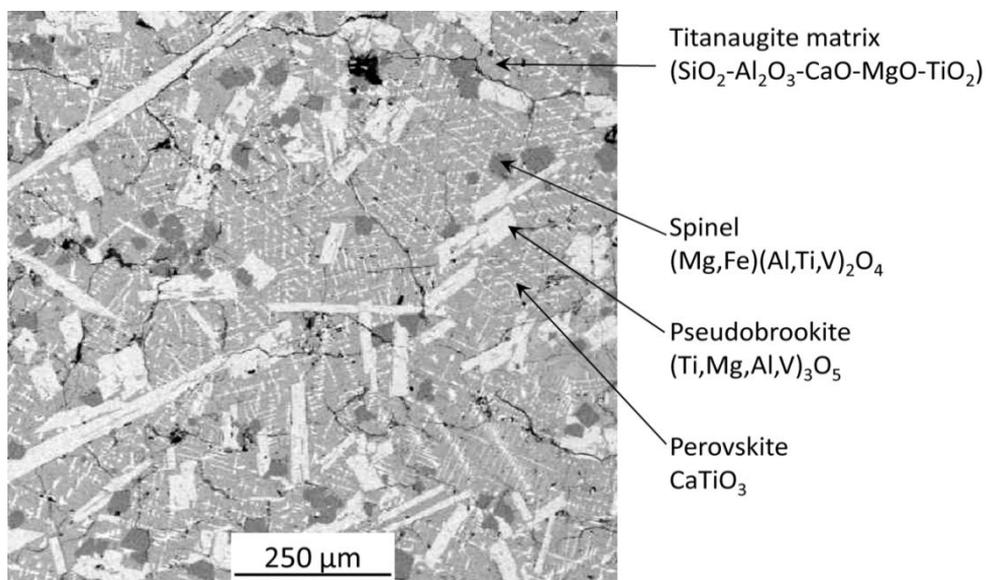


Figure 1: Microstructure (backscattered electron image) of solidified slag; approximate composition 32% TiO_x, 22% SiO₂, 17% CaO, 15% MgO, 14% Al₂O₃ and 0.9% V₂O₅

acid leaching process, followed by purification, titanium hydroxide precipitation and calcination (similar to the sulphate process for TiO_2 pigment) has been described.¹¹ Another process involves the formation of titanium nitride by heating a mixture of slag and carbon under nitrogen to approximately 1300°C , with subsequent low-temperature chlorination (at approximately 200°C), to form TiCl_4 .¹² The complexity of these processes follows directly from the chemical behaviour of titanium; the complexity places such slag-based processes at a cost disadvantage relative to natural ilmenite, which is described as a “low-cost and relatively abundant mineral resource”.² This is emphasized by Figure 2, which gives the cost per contained titanium of ilmenite, high titanium slag, TiO_2 pigment and titanium metal sponge. The feedstock (ilmenite) has a low value compared with the final products; this leaves little scope for complex processing to reprocess by-product slags to generate synthetic feedstocks. The conclusion is that reprocessing such slags to extract titanium oxide is unlikely to be economically viable.

Effect of impurities during calcination of crude zinc oxide

Waelz kiln process overview

In contrast with ilmenite smelting – which increases the TiO_x content of slag by removing the main impurity, FeO – zinc is recovered from by-products such as electric arc furnace dust by targeted removal of the high-value metal (zinc) itself. This is made possible by the specific physical and chemical properties of zinc, which has a high vapour pressure under reducing conditions, but a low vapour pressure under oxidising conditions; see Figure 3.

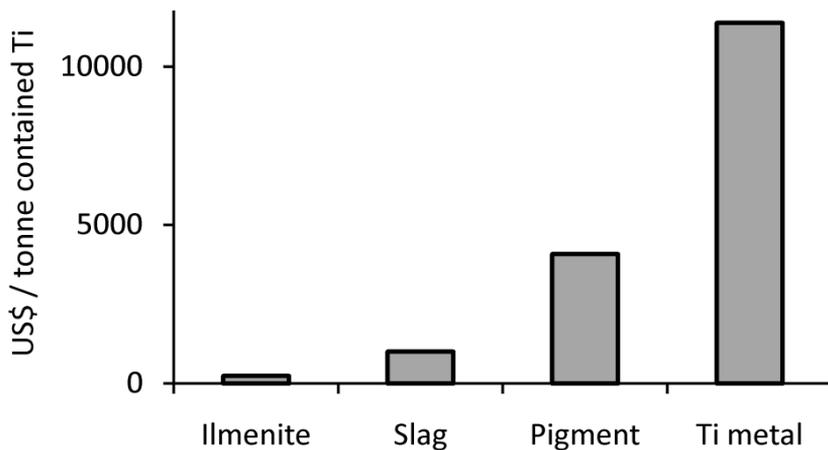


Figure 2: Approximate prices (for the year 2010) of ilmenite, high titanium slag, TiO_2 pigment and Ti metal sponge.¹³

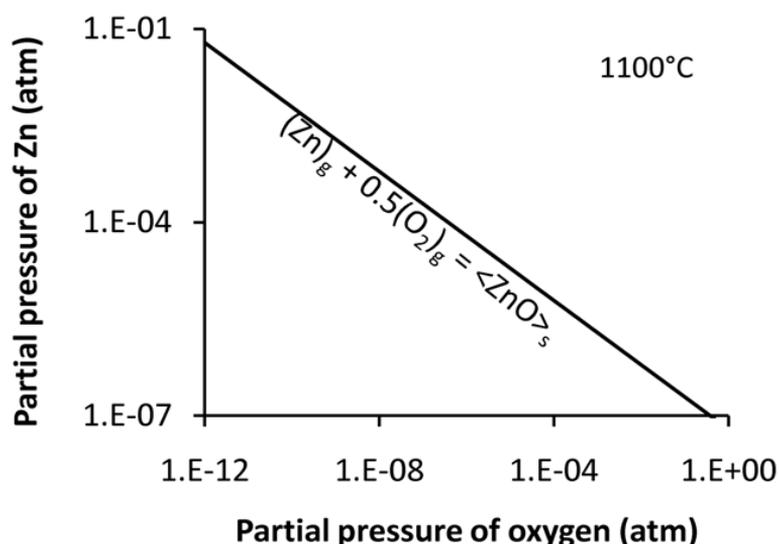


Figure 3: Partial pressure of zinc vapour in equilibrium with pure solid ZnO, for varying O_2 partial pressure (Calculated with FactSage¹⁴)

The strong dependence on oxygen partial pressure and the high zinc vapour pressure under reducing conditions allow manipulation of the vaporisation of zinc. Zinc is fumed off (as metallic zinc) under reducing conditions (typically obtained by adding carbon as a reductant), and zinc is precipitated from the off-gas (as zinc oxide – zincite) simply by making conditions more oxidising.

The Waelz kiln process uses this dependence to process electric arc furnace dust, which typically contains 30-40% Fe, 2-5% Pb, 15-25% Zn, 1-5% Cl and 0.1-0.2% Cd.¹⁵ The dust, together with reductant (coke) and fluxes are fed into a rotary kiln in which zinc and lead are reduced and vaporised (the temperature is around 1100°C); the off-gas is oxidised at the kiln outlet to precipitate the zinc and lead as their oxides.¹⁶ Volatile salts (such as potassium chloride and sodium chloride) also release to the off-gas and collect in the crude zinc oxide (CZO) dust recovered after oxidation of the off-gas.

In the two-stage Waelz kiln process, which was the basis of the study summarised here, the crude zinc oxide is calcined in a second rotary kiln which is operated under oxidising conditions, with a maximum temperature around 1200°C. The zinc oxide does not volatilise in this kiln, but lead chloride and cadmium chloride are removed, and collected from the off-gas as a separate product.¹⁷

As will be described elsewhere in greater detail,¹⁸ accretions which form in the calcination kiln interfere with the movement of material through the kiln. The accretions and the calcine product are similar in appearance and composition; micrographs of calcine particles are given in Figure 4.

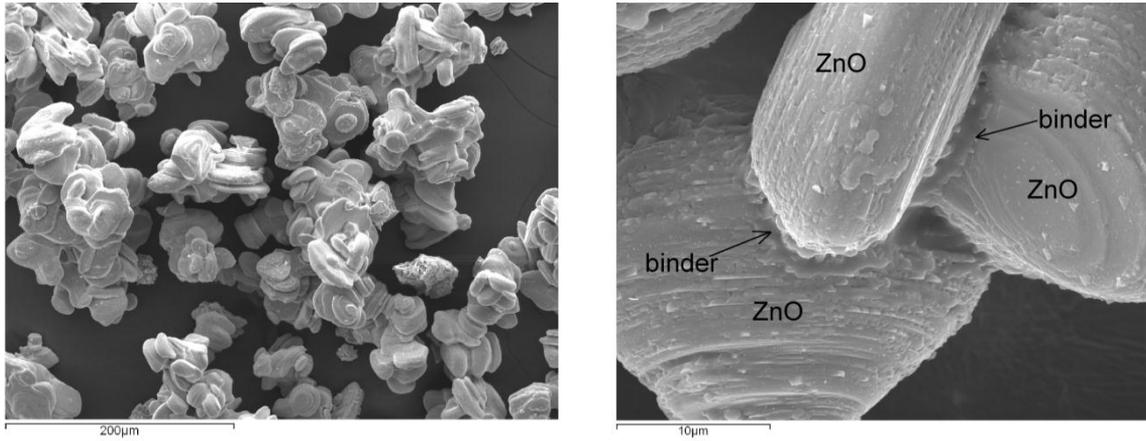


Figure 4: Scanning electron micrographs (secondary electron images), at lower and higher magnifications, of the zincite platelets in the calcined product, showing the presence of a silicate binder phase between the platelets

Calcination converts the zinc oxide dust into platelets. These are cemented together by a silicate phase (Figure 4). Apart from ZnO and a few percent of chloride salts (mainly of lead and cadmium), the crude zinc oxide contains around 1% SiO₂ and 2% CaO. These impurities combine at the calcination temperature to form liquid which dissolves some zinc oxide and iron oxide. This molten phase, which makes up only a few percent of the total calcine volume, is effective at binding the platelets together. The mechanism appears to be similar to that in wet sand, where – if the amount of liquid is just sufficient to fill the surface roughness of sand grains – the strength of the pile of sand increases considerably; see Figure 5. What binds the particles together is the capillary pressure, which arises from the surface tension.

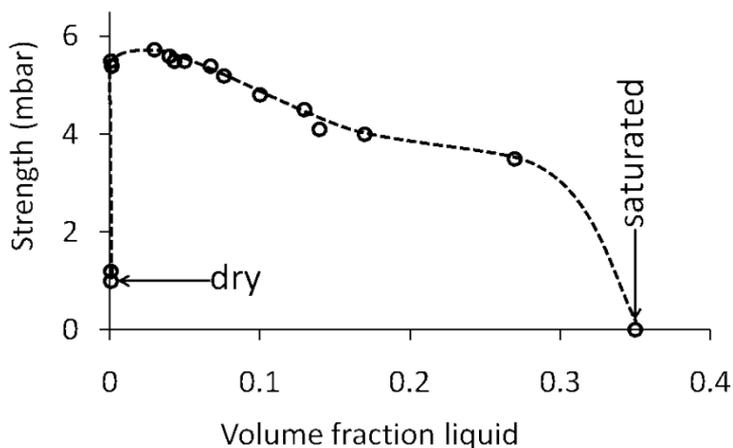


Figure 5: Change in the strength of a packed bed of spheres, when mixed with different amounts of liquid.¹⁹

This “wet-sand” mechanism implies that it would be very difficult to avoid accretion formation in the calcination kiln, since a small volume fraction of liquid is effective at binding the particles together.

Conclusions

These two examples were chosen to illustrate the points that the complexity of slags and dusts strongly affect the technical difficulty (and related cost) of processing these into valuable products, and that the effects of composition are in general quite specific to the process. In the case of titania-rich slags, smelting cannot be used to remove any impurity other than iron oxide; other impurities require combined pyrometallurgical and hydrometallurgical processing (which would generate new by-product streams). In the case of zinc recovery by the Waelz process, minor carry-over of calcia and silica with the zinc vapour results in formation of a small volume fraction of liquid during calcination of crude zinc oxide; this liquid causes agglomeration in the calcination kiln.

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