The Becher Process and Beyond. High Temperature Phase Chemistry of Ilmenite Upgrading

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Australia is the world's largest producer of synthetic rutile, (SR $=TiO_2$), as a feedstock to the multibillion dollar titania pigment industry. Since the late 1960s ilmenite, $FeTiO_3$, has been upgraded to SR in Western Australia by a process developed at the Western Australian Government Chemical Laboratories (WAGCL). It is known as the Becher Process, after its developer, Bob Becher[1] and involves coal reduction of ilmenite to convert the FeO to metallic iron, followed by aeration (accelerated rusting) to remove the iron and produce a +90% TiO_2 product. The phase chemistry was originally described in terms of the Fe-Ti-O system. Reduction according to the ternary system at Becher process conditions should produce a mixture of iron and reduced rutile according to the reaction $FeTiO_3 + (1+x)\ CO \rightarrow Fe(m) + TiO_{2-x} + (1+x)\ CO_2$. Reduction of ilmenite should thus give a 100% upgrade after iron removal. Experience at the first commercial plant (see Figure 1), operated by Western Titanium Ltd at Capel, found that product grade was consistently less than 90% TiO_2. The company contacted CSIRO to conduct research to understand the causes of the poor recovery.

Figure 1. Commercial Becher reduction kiln.

Laboratory studies on plant reduction products showed that the reduced ilmenite phase chemistry did not conform to reactions in the simple ternary system. The ilmenite feedstock used by the company contain MnO and MgO as lattice impurities and they stabilise a phase of composition

M_3O_5. This is a solid solution between anosovite, Ti_3O_5 and $M^{2+}Ti_2O_5$, M^{2+} = Fe, Mg, Mn, and is the main component of acid-soluble titania slags. The M_3O_5 phase locks up FeO in an unreducible form and so limits the product grade. Phase equilibria studies at CSIRO[2] established the stability and composition of the M_3O_5 phase as a function of temperature and reduction potential. Research at the WAGCL led to a modification to the Becher process to neutralise the deleterious effect of MnO, which is the major impurity in WA ilmenites[3]. It involved addition of a sulfur compound during reduction to segregate the Mn as MnS, which is removed using an acid leach. High temperature (HT) phase equilibria studies at CSIRO on the Mn-Fe-Ti-O-S system and its subsystems established the oxygen and sulphur fugacities for formation of the optimal reduced phase assemblage of reduced rutile, metallic iron and MnS[4].

In the early 1990s, the commercial upgrading of ilmenite in WA encountered a new challenge of unacceptably high levels of U and Th in the ilmenite feedstock, which transferred to and concentrated in the SR product. Collaboration between the company and CSIRO led to the development of a new modification to the Becher process to remove these elements and associated radioactivity[5]. It involved the addition of a borate flux during reduction, which penetrated the pores of the reduced ilmenite grains and incorporated the radioactive impurities. These were removed after reduction by leaching the flux. The development of SREP (Synthetic Rutile Enhancement Process) took several years and involved some interesting HT phase equilibria studies to overcome problems encountered during its development. One of these was the formation of an unwanted phase that locked up Th in an unleachable form. The phase is the synthetic equivalent of the mineral loveringite, a Ca titanate that formed by a reaction between the Ca borate flux and the ilmenite. The phase forms at the latter stage of reduction when most of the iron is metallised and a significant fraction of the titanium is reduced to the trivalent state, so that the oxide phase equilibria are reasonably well approximated by the system CaO-MnO-TiO_2-Ti_2O_3. A study of this system as a function of oxygen fugacity was conducted and the stability field of the loveringite-type phase was established [6], see Figure 2.

This knowledge allowed multiple solutions to be presented for elimination of the problem phase. These included operating under more oxidising or more reducing conditions, changing the flux to a low-Ca borate or adding silica to lower the Ca activity. In April 1996 full scale commercial operation of the SREP began successfully, resulting in a lowering of U+Th from +400 ppm to -100 ppm and increasing the SR grade from 90 to 94% TiO_2, see plant log of the SREP startup in Figure 3.

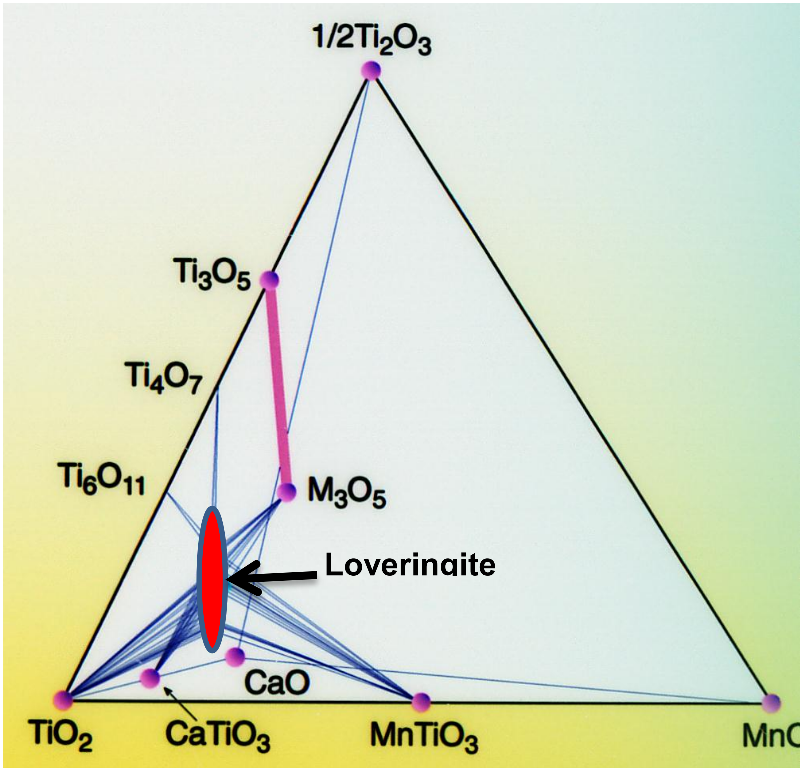

Figure 2. Stability field for loveringite-type phase

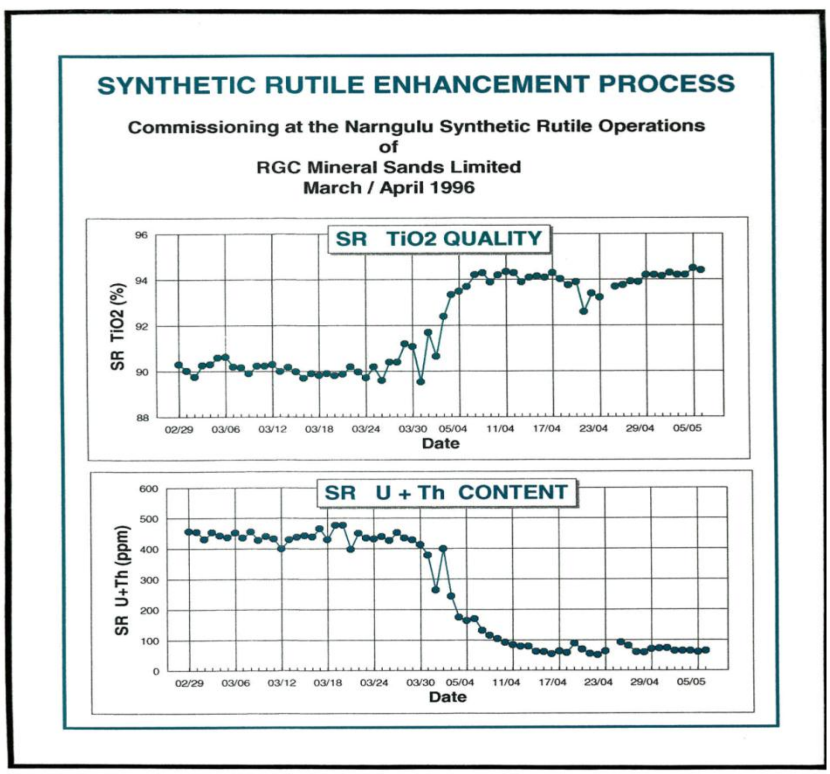

Figure 3. Plant log of the SREP process startup

The Becher process operates at high thoughput rates using secondary ilmenites that are highly weathered and are amenable to HT reduction without sintering. As the weathered ilmenite deposits are being rapidly mined out future feedstocks, particularly from deposits in the Murray Basin, will be more primary. They will also contain higher levels of impurity oxides within the ilmenite lattice, particularly MgO. In anticipation of these changes RGC Mineral Sands started sponsored research at CSIRO in the mid 1990s aimed at developing an alternative to the Becher process for primary ilmenites. Another important consideration was to move away from coal to a more H-rich reductant. The outcome of this collaboration was the development of the NewGenSR process[7]. It involves hydrogen reduction of primary ilmenite, followed by Becher aeration to remove metallic iron and an acid leach to remove a minor Mg-rich ilmenite-type phase. The development of NewGenSR drew heavily on knowledge of the changes in the phase chemistry in the Mg-Fe-Ti-O system as the temperature is lowered. As shown in Figure 4, changing the reduction temperature from a typical Becher operating value of 1100°C, to a lower value of 900°C opens up a new phase field comprising $TiO_2 + M_2O_3 + Fe(m)$, where M_2O_3 is an ilmenite type phase but with strong enrichment of impurity oxides, particularly MgO. This field is readily accessible under suitable hydrogen reduction conditions.

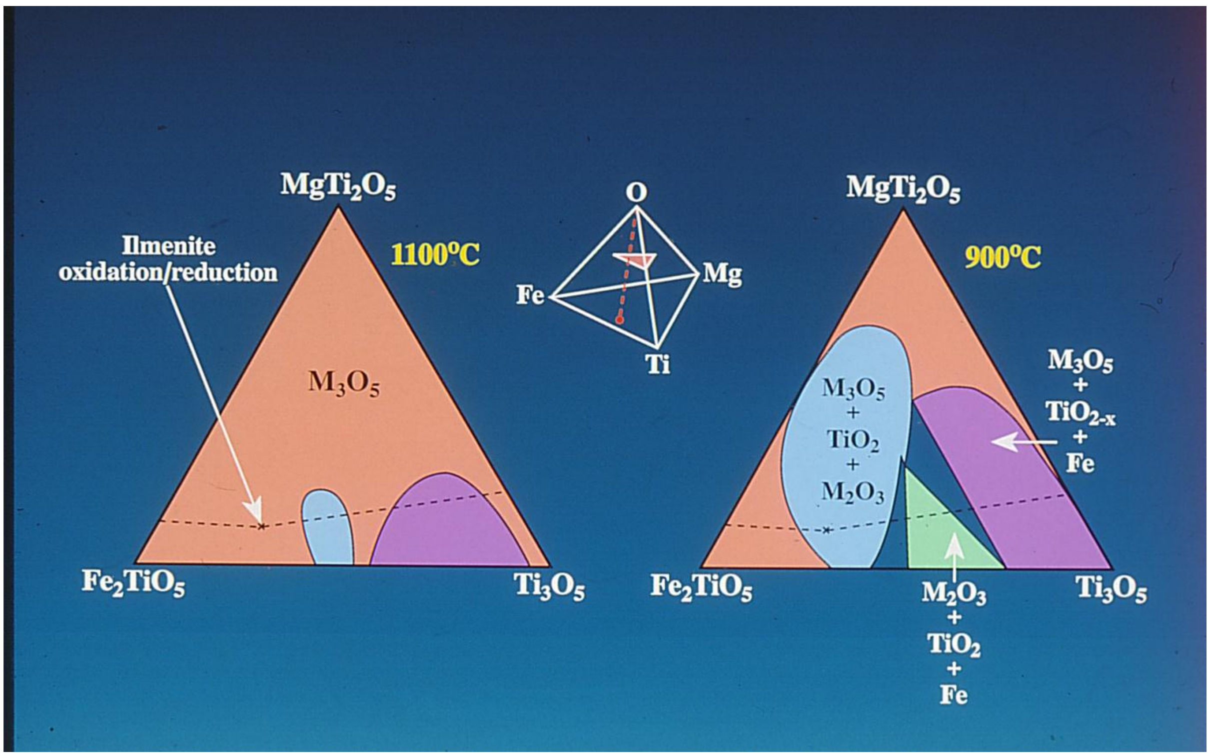

Figure 4. Phase equilibria basis for the NewGenSR process.

The NewGenSR process has been successfully tested at the pilot plant scale by Outokumpu-Lurgi Metallugie (OLM) in Finland, producing an SR with >94% TiO_2. Iluka Resources and OLM made a joint announcement to the ASX in 2002 that they would work together to develop the first NewGenSR commercial plant. The downturn in demand for TiO_2 has postponed this development but it most likely represents the future of ilmenite upgrading.

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