Sustainable Supply of Scandium for the EU Industries from Liquid Iron Chloride Based TiO₂ Plants ‡

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Abstract: Scandium (Sc) applications in solid oxygen fuel cells, aeronautics and heat exchange systems are forecasted to increase significantly without a sufficient continuous Sc supply for Europe. ScaVanger is an EU project for upscaling Sc extraction and purification technologies from various TiO₂ pigment production residues. High purity Sc₂O₃ and ScF₃ will be produced at competitive prices for the EU market. The ScaVanger process is expected to result in a 10% higher production rate and higher product purity as processing starts with a unique cleaning process of actinides. The first plant at a major European TiO₂ pigment production site will be supplying about 30 t/a of Sc₂O₃.

Keywords: scandium; hydrometallurgy; titanium pigment production; metal recovery; metallurgical residues; master alloys; circular economy

1. Introduction

The scandium demand in the EU is expected to rise due to its exceptional physical and chemical properties. The major challenge is a continuous Sc supply chain enabling a massive uptake for producing lightweight, superplastic, high strength, low corrosion and heat resistant AlSc alloys [1]. Scandia stabilised zirconia is increasingly used in solid oxygen fuel cells (SOFC, HTEL) for reaching high fuel performances at relatively lower temperatures [2–4]. Further promising uptakes are expected to rise for heat exchangers and 3D printing [1]. However, Sc is currently 100% imported to EU, mainly from China (66%). Therefore, Sc has been classified as a critical raw material for the future since 2014 by the EU Commission, and several projects (e.g., H2020 SCALE, EIT-KIC ScaVanger) have been launched in the recent years aiming at the implementation of Sc production in the EU from European resources to ensure the supply of this critical metal.
Sc is rarely found concentrated in minerals or ores. Consequently, it is produced mainly as a by-product. Even if found in trace amounts, uranium minerals, nickel laterites and bauxite residue are the promising resources for Sc production in Europe [5]. Moreover, TiO$_2$ pigment production residues have one of the highest potentials to be the main source of Sc for EU.

The European TiO$_2$ pigment plants have a total annual capacity of about 1.5 million tons, providing 20% of the world’s TiO$_2$ production [6]. ScaVanger focusses on iron chloride rich solutions from TiO$_2$ production mainly from high grade TiO$_2$ feedstock (natural rutile, synthetic rutile and upgraded titania slag). Approximately 0.5 million tons of TiO$_2$ pigment is produced via the “chloride process” each year in Europe [7]. These iron rich residual solutions contain exploitable sources of Sc (60–140 mg/L), and also significant quantities of the critical raw materials V and Nb [8,9]. These metal rich solutions are neutralised, dewatered and mainly landfilled as filter cakes at high costs, but also sold to chemical industries without any valorisation of Sc, V and Nb.

At present, only Rio Tinto (Quebec project) plans to produce Sc from TiO$_2$-production residues and Al-Sc alloys for the 3D printing market [10]. In Europe, no process or plant-in-plant exists to convert this waste into valuable products. The objective of ScaVanger is to scale up and integrate a hydrometallurgical process. Furthermore, the project aims at implementing the concept and technology for an “in-line” production of Sc, Nb and V compounds directly from TiO$_2$ pigment production residues. ScaVanger is creating the first Sc production plant in EU (100% market share for Sc). The continuous Sc supply is ensured with sustainable and high-quality processing resulting in a range of products; not only Sc$_2$O$_3$ for SOFCs and ScF$_3$ for the Al-Sc master alloy production, but also Nb-concentrate, V$_2$O$_5$ and V salts (each about 2% of the EU market share). ScaVanger represents a green deal for the EU circular economy concept.

2. Scandium Resources from TiO$_2$ Pigment Production

Sc resources are available in liquid residues from TiO$_2$ pigment production, reaching a total production capacity of 8.4 million tons worldwide [7]. The major Ti pigment production is via the sulphate method in Europe and China. Therefore, hydrolysed sulfuric acid solution from titanium oxide production is considered as a significant source [9]. Consequently, many studies focussed directly on the sulphate method rather than the chloride method. Typically, this residue contains 15–25 ppm Sc. Previous studies showed that both solvent extraction (SX) and ion exchange (IX) with organophosphorus and synergistic reagents can be used to recover Sc [8,9,11]. Even though the focus was given on the sulphate method, about half of the production of TiO$_2$ pigment follows the chloride method [12]. Only in Europe, approximately 665 kt/a TiO$_2$ are produced via this method generating acid residues rich in Fe, Ti in which typically 60–140 ppm Sc is present.

Since many leading European TiO$_2$ pigment plants follow this method, ScaVanger focusses on the chloride process, researching and developing innovative and feasible processes to produce Sc, Nb and V. ScaVanger will create the first industrial “zero-waste” viable concept, flowsheet and plant in Europe. Today in the EU, there are five plants producing TiO$_2$ pigment via the chloride method. This would imply residues of about 450,000 t/a TiO$_2$ pigment production (total EU: 1.5 Mt/a TiO$_2$ production).

3. Scandium Markets

3.1. The Exceptional Properties of Scandium

Sc improves mechanical strength, resistance to thermal cracking, to recrystallisation and reduces grain size in many Al alloys [13–16]. The high strength produced by Sc in Al alloys is mainly due to nanosized Al$_3$Sc crystallites, which form at temperatures of 200–400 °C. These particles are very fine and homogenously distributed [13,17]. Adding Sc to Al has also an anti-recrystallisation effect [1]. This makes Sc one of the most attractive...
alloying elements to be used in high-performance Al alloys, particularly in combination with Zr.

Another major industry where Sc is currently being used is the solid-oxide fuel cells. When Sc replaced Y in solid oxide fuel cells, extreme ion conductivity was observed and high efficiency at relatively lower temperatures was achieved [4,18]. Stationary SOFCs are beginning to be deployed by Bloom Energy Corp., which possess numerous patents for Sc containing SOFCs for many applications [19,20].

Extremely hard ceramics, the second known hardest material after diamond, could be synthesised by inserting ScC into TiC [21]. Moreover, Sc containing laser garnets provide an improved laser performance when used in the optical field [22]. Higher efficiency could be achieved by permitting the transfer of energy efficiently in doped laser garnets. They could also be used in medical applications to cut soft and hard tissues without adverse temperature effects [23,24]. In addition to laser garnets, blending ScI$_3$ and Na in metal-halide lamps could achieve an exceptional lighting source for high colour quality and luminous efficiency [25].

3.2. The Major Scandium Markets and Applications

The aluminium and energy market will take up about 80% of Sc for applications such as 3D printing, electronics, lighting, aerospace and defence, SOFC and ceramic sectors [1,26].

Aeronautic industries need superplastic light Al alloys with strain rates $>10^{-3}$ s$^{-1}$. Such products permit the construction of 15–20% lighter aircrafts, which are more fuel-efficient, thus reducing the CO$_2$ footprint [27]. SOFCs operating with renewable energies use water electrolysis as a non-fossil fuel-based process to produce greener electricity [2]. Among the different technologies used for water electrolysis, high temperature electrolysis (HTEL) or solid oxygen electrolysis is a candidate for Sc use. This new technology is already commercialised, albeit to a very small extent (e.g., Coradia train and Alstom). It uses Y for doping Zr-dioxide electrolytes, necessitating high temperatures between 650 and 850°C to be sufficiently conductive. Sc can replace Y and will significantly reduce the operating temperature and simultaneously increase the mechanical strength and oxygen ion conductivity at constant chemical stability [28]. The market uptake of Sc in this sector is difficult to estimate. Kiemel et al. [2] forecast about 20% market shares by 2050 for HTEL (versus about 40% market shares for AEL and PEMEL, respectively, as HTEL are at a lower developing stage at present). A continuous high-quality Sc supply at a competitive price for a massive uptake in HTEL may contribute to a higher market share of HETL, although Y will stay prevalent.

In general, forecasts for Sc uptake are difficult to make, as they depend highly on massive uptake in non-conventional sectors, such as the SOFCs, HEX and the aerospace industry. At present, the EU consumes about 780 kg of Sc$_2$O$_3$/a (world consumption: about 15 t Sc$_2$O$_3$/a).

3.3. Scandium Suppliers at Present and in Future

In 2012 only three Western scandium projects were identified. Today, there are fifty-seven potential Western scandium suppliers. Australia is well represented with 19 potential scandium suppliers. At present just one Western supplier (SMM) is currently producing scandium oxide as a by-product from a nickel laterite treatment plant.

Ongoing projects at pilot and preindustrial stages have been announced by GSA (UK) announcing Sc extraction from residues out of TiO$_2$ pigment production [29]. Rio Tinto (Quebec) produced the first Sc from by-products of TiO$_2$ pigment production and ScAl master alloys for the 3D printing sector [10]. The US company Anactisis LLC is investigating Sc recovery from fly ash and is in the preindustrial stage with its project [30].

ScaVanger products differ as they will be tailor-made to the end-user needs. Not only high purity Sc$_2$O$_3$, ScF$_3$, but also NbTi alloys and V-salts will be produced in an integrated plant.
3.4. Scandium Products and Price Evolution

The major commercialised Sc form is white Sc₂O₃ powder, as it is stable at room temperature. Its conventional production method includes Sc separation and recovery by SX/IX, Sc oxalate precipitation and calcination of the oxalate precipitate at 700–800 °C. Currently, Sc₂O₃ is the major Sc product and used to synthesise the other Sc derivatives (Sc₂(SO₄)₃, ScF₃, etc.) as well. The price highly depends on the purity of the product and varies between 900 and 3800 $/kg [26].

Scandium fluoride (ScF₃) is the preferred form of Sc by Al-Sc master alloy producers as it can be directly introduced into the molten salt electrolysis to produce Al-Sc alloys. Nevertheless, the production of ScF₃ requires special equipment since it is typically produced via reacting gaseous hydrogen fluoride (HF) with Sc₂O₃, and therefore is the most expensive Sc form. MEAB designed an alternative hydrometallurgical process to produce ScF₃ directly without the need for gaseous HF in the scope of the EU H2020 Scale Project. Similar to the oxide form, purity affects the price of the ScF₃ product which ranges between 1200 and 8000 $/kg [26].

4. The ScaVanger Technology

ScaVanger focuses on generating a unique, feasible and greener process to valorise waste from the chloride method of TiO₂ pigment production. Since, TiO₂ pigment production is an important economic pillar for the EU industries, it will ensure the continuous supply and production of Sc. Moreover, not only the naturally occurring radioactive material (NORM) elements are cleaned from the residual solution, but also valuable by-products (Nb and V) will be produced with the tailored ScaVanger process. ScaVanger will produce both intermediate and refined products for direct use in the alloy industries.

4.1. Metal Extraction from Lab to Pilot from TRL 2 to TRL 5-6

Within the EU H2020 SCALE project, an SX process has been developed which bypasses the Sc oxalate precipitation and calcination to form Sc₂O₃ and eliminates the fluorination method via HF vapour to produce ScF₃. In this hydrometallurgical method, ammonium fluoride (NH₄F) is used in the SX process which results in (NH₄)₃ScF₆ product. Both, ScF₃ and Sc₂O₃, can be synthesised from this intermediate product without complex processing or special equipment [31,32]. The process has been tested in a continuous mixer settler operation over more than four weeks at MEAB, Germany. Based on the outcome of the pilot plant demonstration and the design throughput of the pilot plant used at MEAB, the capacity of Sc was calculated to be 20 g/h, or 1 kg/day of ScF₃. This innovative process was tested with various secondary sources: bauxite residue leachates, TiO₂ pigment production acid residues, end-of-life products and Sc concentrates [33,34].

Although the element of interest is Sc, two additional critical metals could be produced as by-products. SX for V extraction has been developed in low acidity media (sulfuric and hydrochloric) at ORANO Mining (2017–2019) to process Niger’s U plant effluent (COMINAK) and tested successfully over a total of three weeks’ continuous operation of a mixer-settler pilot unit. Adaptation to a nitric environment is in progress (TRL 5-6). Nb will be extracted via chemical precipitation of a mixed hydroxide of Nb-Ti(-Al-Cr-Zr) (TRL 4-5) and subject to repeated washing for optimal removal of soluble salts.

The process chain consisting of calcination, self-propagating high temperature synthesis (SHS) process and electron beam melting (EBM) will be demonstrated first at TRL 5 for parameter optimisation for the production of Nb-Ti alloys. Using new input material in this process chain, all TRL levels up to TRL 6 will be run through again to confirm the implementation of the production method developed. If successful, upscaling to TRL 7 will be performed in further project schedule. This means a minimum production of 400 kg metal oxides per week for the calcination step, 200 kg of high entropy alloy (HEA) via SHS-process per week as well as 100 kg of refined target alloy by EB melting. Al-Sc master alloy production (+Nb-alloys) reached TRL 5 by RWTH-IME.
To achieve a highly clean product, radioactive elements will be removed from the feed. U-Th removal is well-established using IX and SX units, currently employed, for example, in Kazakhstan, Canada or Central Africa by ORANO Mining.

4.2. From Pilot to Industrial Scale TRL5-6 to TRL 8-9 (Go-to-Market)

The innovative process starts with the recovery and purification of Sc via hydrometallurgical routes. After the extraction process the Sc-depleted solution is then treated with a boil-and-bake process to remove the elements of interest. During boil-and-bake, in addition to the recycling of the water, most of the free HCl is also recovered by evaporation and condensation during boiling and baking stages. The major constituents of the residual solution remain soluble while the target metals form oxides or oxychlorides. Therefore, upon the addition of water, major impurities can be dissolved while Nb and V stay in the residue and can be further processed from the residue. A simplified process flow diagram proposed by ScaVanger is presented in Figure 1.

Figure 1. Conceptual process flow sheet of ScaVanger.

The by-products of this treatment, Nb-Ti oxides, will be produced through calcination. The gained oxides will be treated in an aluminothermic reduction to produce Nb-Ti alloy, a time and cost-reducing process compared to the traditional Nb alloy production technology [35]. V-sodium and/or V-Fe salts, and V$_2$O$_5$ will be produced through application of very selective and unconventional bio-degradable extractants to reach purities of >99% of V.

ScaVanger’s innovative breakthrough in Sc (+V, Nb) production lies in the smart combination of these steps using special reagents and additives to produce Sc (Nb, V) compounds of unique properties. High purity and unique chemical properties can be tailored to meet customer requirements. The remaining harmless solutions (no more NORM) can be sold as iron-rich solutions, or will be ready to produce, for example, Ca-nitrates (e.g., thermal energy storage, medical sector, fertiliser) and Mn-Fe oxyhydroxides.
(e.g., water treatment), while the remaining water can be recycled in the plant to reach zero liquid discharge for a circular society (Figure 2).

Figure 2. Zero-waste ScaVanger concept.

4.3. ScaVanger as Business Partner

Due to the flexible and versatile ScaVanger approach and its promising business cases, three main business partnership models are feasible (Figure 3).

First, on-site Sc-intermediate product extraction in the TiO$_2$ production industry is conceivable. The possible option on the left of Figure 3 shows the complete inhouse production of Sc, V and Nb which entails residue valorisation. TiO$_2$-enterprises already sell
residual streams to generate income from it. With the presented ScaVanger technology the profitability of this source of income could be extended with the production of Sc. Due to the steadily tightening of EU regulations regarding the minimisation of hazardous residues, the presented approach, thus, provides economic incentives in addition to ecological benefits by analysing residual streams and reducing problematic compounds. Finally, short distances and the opening of new and developing markets are other benefits from an integrated Sc production.

Second, the technology presented can also be directly utilised in manufacturing, such as by the alloy or the SOFC industries. The model (Figure 3, middle) shows this option with the connection to the TiO$_2$ industry, visualised by the arrow representing the residual streams required as input material. Sc may/will be a crucial substance in the future for this interest group regarding prices and product quality. No supplier dependency, custom tailored materials and risk reduction are in general advantageous implications of in-house manufacturing.

Lastly, a ScaVanger start-up company for intermediate and refined Sc-product manufacturing with a sole focus on Sc, V and Nb production out of residual streams could be another business option. Experiences and findings of this project as well as of the SCALE project have shown high complexity in metallurgical processing. Thus, specialisation regarding extraction from residual streams could be helpful for TiO$_2$ producers as for market players. Preliminary business cases have shown reliable revenues, and therefore, a sustainable return on investment over lifetime in all scenarios considered. Despite this, external investment, as illustrated in the right diagram of Figure 3, for the ramp-up process and the establishment of the ScaVanger company would be necessary.

All three approaches underpin the idea of a more sustainable and independent supply with the critical material Sc. As already mentioned, the ScaVanger approach contributes to the EU circular economy concept and thereby to a more sustainable and efficient industry. In addition to sustainability aspects that is accounted in the project, the production process for these metals is aimed to be transparent, which is rarely given in current metal supply chains [36]. Furthermore, the current dependency of the EU, especially on China, involves risks regarding a continuous and stable supply of materials due to possible political conflicts. This risk would be eliminated with EU based Sc production facilities.

Within the research project ScaVanger, all business opportunities will be further examined and a real-scale demonstration of ScaVanger processing will be performed at a European TiO$_2$ pigment production site. For full industrialisation, the plant design and installation will be performed by MEAB within three years after the project (2026), followed by a half year test and stabilisation phase.

5. Outlook

- A massive uptake potential of Sc in electricity producing technologies (SOFC, SOEC), heat exchanger and aircraft sectors necessitates continuous, high-quality Sc production in form of intermediate and refined Sc products in Europe at competitive prices compared to China.
- There is a significant potential in the EU for Sc production from TiO$_2$ pigment production. The complete Sc need for various markets could be supplied from this promising source.
- The Sc resource from TiO$_2$ pigment production residues depends on the evolution of the TiO$_2$ market. It can be expected that no new TiO$_2$ producer arrives on the European market despite forecasts for a global increase in TiO$_2$ oxide production. TiO$_2$ production from the chloride method can be considered constant and remains a reliable and continuous sustainable Sc source.
- The innovative ScaVanger processing method proposes a complete, feasible, greener and adaptable process for simultaneous Sc, Nb and V compound manufacturing since the supply of these elements is critical for the future. ScaVanger can be classified as a zero-waste generating process.
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