Proceeding Paper
The Future of Scandium Recovery from Wastes †

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†   Presented at the International Conference on Raw Materials and Circular Economy, Athens, Greece,
     5–9 September 2021.

Abstract: With growing demand for renewable and clean energy technologies, the need in rare earth metals is increasing. Scandium, which is often considered a rare earth element (REE), is a critical metal mainly used in solid oxide fuel cells (SOFCs) and high strength aluminum alloys used in aerospace and 3D printing applications. Furthermore, scandium supply is limited due to its scarcity and the high cost of its production in Asia and Russia while Europe has no production of scandium. Therefore, scandium extraction from alternative resources such as secondary resources located in Europe is of great concern. Within this context, this work provides a condensed state-of-art review of the issue of scandium recovery from industrial wastes. Priority was given to addressing the technological and economic challenges associated with the recovery of scandium from the said residues, with particular emphasis on the bauxite residue from alumina production, which represents nearly 5 million tons on dry basis per year in Europe.

Keywords: hydrometallurgy; complex processing; secondary resources; coal ash

1. Introduction

Scandium is a transition metal mostly used in a developing technology of solid oxide fuel cells (SOFCs) and Sc-Al alloys. In the year of 2017, scandium entered the list of critical raw materials (CRMs), assessed separately from the rest of rare earth elements (REEs). According to Dittrich and Yagmurlu [1], the world production of scandium as of 2018 was mostly concentrated in three countries: China (66%), Russia (26%) and Ukraine (7%). Because of the scarcity of deposits containing high concentration of scandium, the absence of its mining and production on the territory of the EU and virtually no recycling from end-of-life products [2], scandium is characterized with a relatively high supply risk [3]. Regarding substitution, there are several options, for example, scandium can be replaced by yttrium in SOFCs and by titanium and lithium in Sc-Al alloys. It has to be noted, however, that yttrium, titanium, and lithium all belong to CRMs as well [4].

One possible way of avoiding a potential supply disruption of scandium is finding alternative sources. Secondary sources, such as some industrial residues, present a promising potential for scandium recovery. Industrial residues characterized with relatively high scandium content include ashes, generated during coal combustion and bauxite residues, containing on average 2.9 and 11.6 times the average concentration of scandium in ores [5]. Nevertheless, despite the attractive concentrations and large available tonnages of these residues, the extraction of scandium from them presents significant technological and economic challenges.

2. Background

According to the European Commission [4], "scandium is not traded on any metals exchange, and there are no terminal or futures markets where buyers and sellers can fix an

official price. Scandium products are sold between private parties at undisclosed prices". The U.S. Geological Survey [6–8] has reported the variation of the price of scandium oxide between 2010 and 2020 (Figure 1). According to these data, in the period of 2018–2020 alone, the price of scandium oxide (99.99% purity) dropped by 17.4%, and by almost 30% from the year 2014, when the peak price was reported. The high price of scandium stems from complexity in extraction and limited world production; this partially justifies the expectations of the metal market price reduction in case of a supply increase. It is evident that the price volatility of scandium will affect the profitability of its extraction from residues. It is, thus, possible that the currently developing technologies targeting exclusively scandium will render unprofitable upon the market adjustment to the larger available tonnage. Hence, a technology allowing to produce multiple products from residues must be considered to ensure the financial security of the re-processing operation.

Figure 1. Price of scandium oxide US$/kg, data from [6–8].

Apart from being economically viable, the re-processing technology must exhibit low environmental footprint; consequently, the development of technologies allowing comprehensive utilization of the residues gains its momentum worldwide. The zero-waste and low-carbon emission concepts are intensively promoted to assure the sustainability of the re-processing. Another very important concept stimulating today's research progress is the concept of circular economy. Near-zero-waste and circular economy concepts are sometimes confused. It has to be mentioned that these concepts are not contradictory. While both are greatly oriented towards preservation of environment and smart resource utilization, circular economy is designed around the thought of keeping the materials in the supply chain, contrary to simply minimizing the waste disposal (near-zero-waste). Therefore, priority is given to technologies allowing, in the first place, to extract metal values from the residue and to return it into the loop, rather than to re-utilize the residue as bulk material (almost as is) in the construction industry, for example.

In the past 20 years, significant research addressed the problem of scandium recovery from industrial residues; the majority of these studies, however, is characterized with low technology readiness level (TRL), meaning that tests were mostly conducted at laboratory scale (TRL 4). Nevertheless, that research offers a valuable insight of the potential technological problems and bottlenecks to look out for while designing a process for metal recovery from residues. Below, the main technological and environmental challenges encountered in the literature addressing re-processing of bauxite residue and coal ash are reported. The review only concerned the technologies allowing the recovery of scandium as one of the final products of the operation.

3. Bauxite Residue

Bauxite residue (BR) is waste generated during alumina production via the Bayer process. Gräfe et al. [9] examined 63 BR samples and reported an average major

constituent composition of the BR (Table 1), the data represents an average $\pm$ standard deviation of the population.

Table 1. Major constituents of bauxite residues [9].

Constituent	Average Content, %
Fe_2O_3	40.9 ± 15.6
Al_2O_3	16.3 ± 6.4
SiO_2	9.6 ± 6.7
TiO_2	8.8 ± 4.4
CaO	8.6 ± 9.4
Na_2O	4.5 ± 3.3
Loss of ignition	10 ± 2.8

The average pH of the untreated residue liquor is 11.3 ± 1.0; the particle size distribution is between 100 nm and 200 μm [9]. The content of scandium in the BR varies depending on the origin of the bauxite and the parameters of the Bayer process. The scandium content in bauxite residues of different origin is reported in Table 2.

Table 2. Scandium content in the bauxite residues of different origin [10–13].

Residue Origin	Scandium Content, ppm
Greece	121
Australia	54
Canada	31
China	158
Hungary	80
India	58
Russia	73–228
Jamaica	98–112

It has been reported [10,11,14–16] that scandium in BR is associated with Ti and Fe phases, and often occurs as a replacement in the lattice matrix of Fe(III) oxide or FeO(OH). Therefore, in order to achieve acceptable scandium extraction, dissolution or transformation of Sc-containing phases is required.

Common issues encountered during the direct acid leaching of BR with mineral acids include: (1) low extraction of Sc while using non-concentrated acids, and (2) high co-extraction of other elements (e.g., Fe, Si, Al, Na and others) while using concentrated acids [11,17–19]. Another problem frequently encountered while applying concentrated acids directly to BR is the dissolution of silica followed by the formation of silica gel. This may lead to issues in downstream operations, such as, for example, significantly reduced efficiency of filtration. To resolve this problem, several technologies allowing to prevent the formation of silica gel were developed, such as dry digestion [16], sulfation–roasting–leaching [20], concentrated sulfuric acid leaching at elevated temperatures [17], and direct leaching with ionic liquids [21,22].

Selectivity between scandium and iron phases can be achieved through applying what is called the "complex processing". Complex processing is a combination of pyro- and hydrometallurgical methods in the same flowsheet designed for recovery of metal values from the residue [23]. Examples of such technologies include sulfation–roasting–leaching [20], ammonium sulfate roasting followed by ultrapure water leaching [24], acid baking followed by water leaching [10], reductive roasting and magnetic separation followed by the phosphoric acid leaching of non-magnetic fraction and alkali leaching [25–27].

Commonly reported ways to extract scandium from the BR leachates include solvent extraction using such extractants as P204 (bis-2-ethylhexyl phosphoric acid), P507 (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester), P350 (di-(1-methyl-heptyl) methyl

phosphonate) and TBP (tri-n-butylphosphate), ion exchange resins and adsorption materials [28,29]. An important challenge raising at the extraction step is generation of dilute leachates with low concentration of scandium ions [30,31], which is known to be problematic for subsequent liquid-liquid extraction process. In order to address this issue, several methods were developed at laboratory scale, including extraction with ionic liquids [31] or supported ionic liquid phase [30], solid-liquid extraction with mesoporous silica [32], and precipitation-leaching [28]. In addition, the pre-concentration or purification of the leachate though major impurity removal with resins (adsorption and ion exchange) has been reported by Zhang et al. and Zhou et al. [33,34].

As it was stated before, BR is characterized with high alkalinity. This is not only problematic from an environmental point of view (e.g., due to unsafe disposal), but also from the point of view of re-processing, mainly, because of the high acid consumption during the leaching process. A systematic study conducted by Borra et al. [11] on direct acid leaching of bauxite residue with organic and mineral acids has demonstrated that water washing of BR prior to leaching is not feasible. The team performed four consecutive washing operations using fresh water at liquid to solid ratio as high as 50:1. Nevertheless, even after four washes, the pH remained around 10, which was explained by the buffering properties of the BR. Rivera et al. [15] reduced acid consumption during leaching by partial neutralization of the bauxite residue with carbon dioxide prior to leaching; however, Sc extraction did not improve significantly, and in highly neutralized BR it even decreased. It was also reported [9] that neutralization of BR can be achieved by using SO_2 or microorganisms.

Fine particle size of BR, on one hand, can be beneficial for the leaching kinetics due to the high surface area available for the reaction with leaching solutions. On the other hand, fine particle management can be a complex task. Filtering and other solid–liquid separation operations can be negatively impacted by fine particles. Recycling of liquids brought in contact with the residue can be complicated due to contamination with fine particles. In aqueous solutions, a combination of fine particle size and high alkalinity can promote negative charging of the particle surfaces, hindering inter-particle coagulation through electrostatic mechanisms [9] and, thus, decreasing the liquid–solid separation rate and efficiency. In the latter case, the ionic strength of the solution plays a great role. Additionally, the chemistry-dependent rheology of fine particle suspensions has to be considered as an important parameter for process design.

4. Coal Ash

Coal ash originates from coal combustion in thermal power generation plants. This residue is commonly present in two forms: coal fly ash (found in the dust collector after combustion) and coal bottom ash (residue found in the bottom and on the walls of the incinerator). Coal ashes are mainly composed of SiO_2, Fe_2O_3, Al_2O_3, CaO, K_2O, TiO_2, MgO, P_2O_5 and residual unburned organic matter. The quantity of scandium that can be found in the ashes varies in function of coal origin [35–37]. Park et al. [38] reported Sc concentration in the Korean fly and bottom ashes to be 63.9 ± 5.5 ppm and 54.4 ± 5.7 ppm, respectively. US fly ashes were reported to contain 1 to 4 times the content of scandium in the upper continental crust, with mean values per basin varying between 24 and 38.5 ppm [37]. Arbuzov et al. [35] reported scandium contents in the ashes resulting from the coals found in the Siberia, the Russian Far East, Mongolia, Kazakhstan and Iran (Table 3).

It must be noted that the process parameters influence the phase transformation occurring in coals during combustion. It was demonstrated that, if present, REE-bearing apatite, zircon, monazite and xenotime go through no or very little change during coal combustion, whereas hydrated REE-bearing phosphates convert into their anhydrous form [39]; REE-organic complexes and REE(-bearing) carbonates decompose to REE(-bearing) oxides. Monazite shattering (grain fragmentation) can occur upon rapid heating to 1400 °C [39,40], without chemical change of the mineral; in the presence of CaO melting temperature of monazite can decrease to as low as 600 °C leading to formation of REE oxides. It is possible

that REE(-bearing) oxides formed during combustion diffuse in the aluminosilicate glass phase, ending up dispersed throughout the phase [39].

Table 3. Scandium content in the coal ashes reported by [35].

Residue Origin	Scandium Content, ppm		
	Min	Max	Mean
Siberian region	9.8	150	19.2–43.3
Russian Far East region	10.9	60.3	15.4–28.9
Kazakhstan	23	79.7	32.7–46.3
Mongolia	7.3	78.4	15.6–49.9
Iran	33.1	63.9	48.3

The discussion about scandium-bearing phases in the coal ashes is still open; it was suggested that scandium in ash is associated with Al_2O_3, present in the form of alumosilicates, clay minerals [36]. At the same time, Arbuzov et al. [35] suggested that in some *coals*, scandium cannot be entirely associated with clays, proposing that a part of scandium is associated with the organic matter; after ashing (laboratory, at 800 °C) scandium was found in Sc-containing zircon or zircon minerals of complex composition in an aluminium–silicate matrix or in slaggy aggregates of complex composition (Si, Zr, Al, Ca, Ti, V, Cr, Fe, Ni, O). The same study reported occurrence of Sc-containing xenotime in the coal sample, prior to ashing. Park et al. [38] found that most scandium dissolved during the last step of Tessier sequential extraction (using hydrofluoric and nitric acids under high temperature and pressure) and the last step of European Community Bureau of Reference sequential extraction (mixture of hydrochloric acid and nitric acid at elevated temperatures) indicating that scandium in the ashes was strongly bound in crystalline structures. A significant portion of other REEs was also extracted in this last extraction step, which explains the necessity of using strong acids for the recovery of REEs from fly ashes.

Some processes allowing extraction of REEs from coal ashes have reached the commercialization level [41,42]. Companies, such as RockTron, Expansion Energy and PSI Corp are conducting research and suggesting options for coal ash processing designed to extract REEs. Elixsys proposes a process involving ash leaching, precipitation, concentration and separation allowing to produce misch metal (REE alloy). Several pilot-plant projects were launched in the US aiming to extract REEs from coal and coal by-products. For example, the University of Kentucky proposed a process involving flotation, ion exchange and solvent extraction allowing to produce a concentrate with 2 wt % of REEs [43]. Physical Sciences Inc. (PSI), Center for Applied Energy Research (CAER), and Winner Water Services, LLC (WWS) united their efforts to extract REEs from coal ash; the teams suggested a flowsheet combining physical (froth flotation, magnetic separation) and chemical separation stages (digestion, solvent extraction) for the production of two separate concentrates: Sc-rich concentrate and REE-rich concentrate. Hower et al. [44] described the physical separation process in which the froth flotation was used to retrieve the carbon matter, the flotation tailings were directed to magnetic separation to remove iron-containing magnetic particles, after which the non-magnetic fraction was screened at 75 μm. It was found that relative to the feed (containing 26 ppm of Sc), the carbon-containing fraction and the non-magnetic −75 μm fraction were slightly enriched in scandium, containing 34 and 29 ppm of Sc, respectively. Similar findings (i.e., size fraction-dependent REE enrichment) were reported by Lin et al. [45]. Application of magnetic separation for REE enrichment from previously untreated coal ash has given mixed results, which could be related to the presence of REEs (including Sc) in both, non-magnetic, and magnetic/paramagnetic phases (e.g., xenotime and monazite); the degree of liberation of the aforementioned phases affects the separation efficiency as well.

Physical separation methods, such as gravity concentration (excluding heavy liquids) and magnetic separation have often lower environmental impact than hydrometallurgical

processing. Hence, the main challenge to overcome by conventional leaching techniques is related to reducing the environmental impact of the process. Nonetheless, some common technological challenges such as selective extraction of REEs over major coal ash components and suppressing silica gel formation are encountered as well. The typical size distribution of coal fly ash is between 1 and 150 μm [45], justifying the preferential use of "wet" processing technologies (e.g., wet magnetic separation, flotation, leaching) over "dry" ones (e.g., dry magnetic separation).

Some more recent processes such as chemical roasting coupled with water and acid leaching [46] and treatment with ionic liquids [47] are in development, suggesting further potential for utilization of coal fly ash as an additional source of REEs (including Sc) in the future.

5. Conclusions

In this work, a brief summary of the economic and technological challenges and bottlenecks related to recovery of scandium form some industrial residues was given. The following major challenges to consider while designing the process for re-treatment of the residues with elevated concentration of scandium were reported: (1) for both, bauxite residue and coal ashes:

1. selectivity between major (e.g., Fe, Al, Si) and trace (e.g., Sc, REEs) components;
2. achievement of acceptable scandium extraction and recovery;
3. silica gel formation;
4. fine particle management;
5. environmental impact of re-processing;

And (2) for bauxite residue specifically:

1. generation of dilute leachates with low scandium concentration;
2. alkalinity of the residue.

From the environmental and circular economy perspectives, these industrial residues must be at least partially recycled. Indubitably, the extraction of scandium alone from BR or coal ashes cannot justify the economic and environmental risks. While intensive research on bauxite residue reprocessing is ongoing, it is characterized with a clear lack of high-TRL studies (>4).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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