

Solid-state Conversion of Scandium Phosphate to Oxide with Sodium Compounds

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Abstract

The market size and demand for scandium (Sc) is increasing in the world due to emerging applications despite the element's high price. Sc is typically obtained as a by-product from various sources; i.e. uranium processing, TiO₂ pigment production, etc., where bauxite residue can also be counted as one of the promising secondary sources to recover Sc. Previous studies showed that it is achievable to precipitate Sc selectively from bauxite residue leach solutions by using dibasic phosphates. To process and purify the resulting concentrate with minimum effort during further operations, scandium phosphate precipitates are tested to be converted into different compounds through a solid-state reaction with sodium hydroxide and sodium salts at varying temperatures. Although the reaction is not kinetically favoured even at 900 °C with salts having high melting points (T_m) such as Na₂SO₄, Na₂CO₃ and NaCl, successful transformation was observed at temperatures as low as 300-350 °C with sodium compounds having low T_m such as NaOH and NaNO₃. The conversion from scandium phosphate into mixed oxide eliminates the phosphorus-containing moieties, thereby favouring the further processing and purification.

Introduction

Since there is a direct relation between the weight of the vehicles and their energy consumption in transport applications, the drive to reduce the carbon dioxide emissions puts lightweight metals and alloys under spotlight.¹ One of the promising candidates of light-weight alloys is Al-Sc alloys, where scandium (Sc) is used as a tuning metal.²⁻⁴ While improved strength, thermal resistance and weldability can be achieved in aluminium alloys with minor additions of Sc, enhanced oxygen-ion conductivity can also be attained in solid-oxide fuel cells.⁵ Hence, scandium was classified recently as a critical metal for future, owing to the steep increase in demand, despite its high price.⁶

Unfortunately, primary Sc ores can be found scarcely in nature and it is synthesised from secondary raw materials or by-products of uranium, nickel laterite or

titanium pigment processing in general.⁷ Bauxite residue (i.e. red mud) is the stockpiled by-product obtained throughout the Bayer Process, having approximately four billion tonnes with previously reported an annual production of 108 to 160 million tonnes. This alkaline waste can be considered as a valuable resource because of its metal content (Fe, Al, Ti, Sc, REEs, etc.).^{8,9} Therefore, complete or partial valorisation of red mud has been in the focus of great interest.

In recent years, complete or partial recovery of Sc from bauxite residue was reported to be achieved mainly by solvent extraction, ion exchange or the combination of these two techniques as a result of the low concentration in the leachates.¹⁰⁻¹³ However, Fe, Al and Ti, co-extraction during these hydrometallurgical operations became a problem and intensive purification was required to produce a high quality product. Hence, more selective and advanced ways mainly to isolate scandium from iron were developed in the laboratory scale. Supported ionic liquids (SILP), ion exchange with inorganic phosphates as well as successive precipitation process with dibasic phosphates are the typical examples for more advanced processes to concentrate scandium while minimizing the other impurities.¹⁴⁻¹⁷

Previously, a three-staged precipitation process was designed.¹⁸ The process is based on selective iron removal step by an aqueous NH_3 solution, since iron is the most problematic element during scandium processing, and successive selective Sc precipitation as phosphate by $(\text{NH}_4)_2\text{HPO}_4$. The obtained concentrate, rich in scandium phosphate has limited applications and must be converted into other forms. The conversion from scandium phosphate into scandium oxide or mixed oxide eliminates the phosphorus-containing moieties, thereby favouring the further processing and purification. In this study, scandium phosphate precipitates are tested to be converted into different salts through a solid-state reaction with sodium compounds at varying temperatures. The designed process scandium phosphate synthesis and conversion is shown in Figure 1.

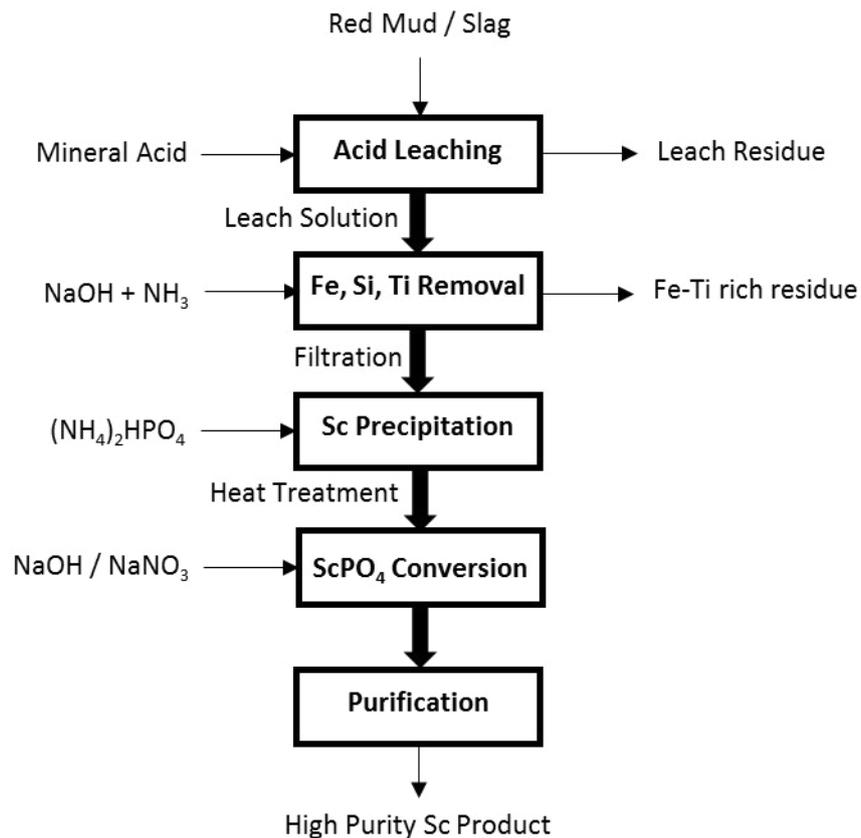


Figure 1. Designated block flow diagram for ScPO₄ synthesis from bauxite residue/bauxite residue slag

Material and Methods

Phosphate precipitation

Scandium phosphate (ScPO₄) was obtained by precipitation reaction. To a 1 M solution of scandium sulphate, 1 M ammonium dihydrogen phosphate solution was added drop-wise under magnetic stirring until the solution pH reached 2.5. The precipitated slurry was filtered and washed with water. The obtained phosphate salts were dried in an oven at 100 °C overnight.

Conversion of ScPO₄ by sodium compounds

ScPO₄ was mixed with stoichiometric amount of sodium compounds (including NaOH, NaCl, NaNO₃ and Na₂SO₄) using a mortar and pestle, and then transferred to a ceramic crucible. The composition of ScPO₄ was assumed to be ScPO₄ for easier calculation. The conversion of ScPO₄ was done by heating the reaction mixture under atmospheric conditions at 300, 350, 750 and 900 °C for 1 h. The temperature intervals were selected based on the melting points and decomposition temperatures of the sodium compounds used.

Characterisation of the product

Thermal behaviors of the samples were determined with differential thermal analysis (DTA) by NETZSCH STA 409CD. All samples were tested under argon atmosphere and heated from 25 °C to 1200 °C with a heating rate of 10 °C/min. Powder X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PW3710 MPD diffractometer coupled with a PW3020 vertical goniometer in Bragg-Brentano geometry. X-ray radiation was sourced from monochromatic CuK α line ($\lambda=1.54056$ Å) operating at 40 kV and 40 mA. The morphology and composition of the products were examined using a Hitachi S-4800 FE-SEM (field-emission scanning electron microscopy) coupled with an Oxford INCA 350 Energy spectrometer, after coating with a 3-nm layer of Pd-Au by sputtering.

Result and Discussion

It was previously reported that, with successive selective precipitation route, more than 90% of the iron in the system can be removed while keeping Sc in the aqueous solution. After this removal step, with the introduction of the dibasic phosphates at certain pH values, Sc can be selectively precipitated as in the form of phosphates. Since the phosphate form of Sc is not preferred in applications which are being developed, converting it into another form, oxide or mixed oxide, is required. For this purpose, synthesised solid ScPO₄ was reacted with different sodium compounds to produce highly favoured sodium phosphate while converting Sc into reacted forms.

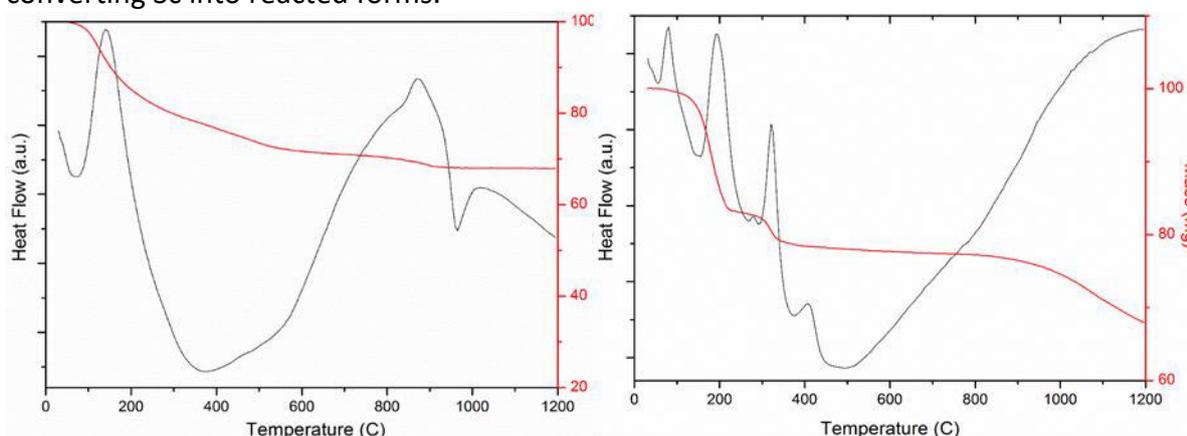


Figure 2. DTA Scans of both ScPO₄ particles (left) and ScPO₄-NaOH mixture (right)

The hypothesis first tested under differential thermal analysis by reacting ScPO₄ particles with stoichiometric amount of NaOH under argon gas. Figure 2 shows the different thermal behaviour upon heating between ScPO₄ (left) and ScPO₄-NaOH mixture (right). As it can be seen from the Figure 2 (left), above 100 °C, chemically bound water was removed from ScPO₄ which is then followed with the pyrophosphate formation starting around 850 °C. When NaOH was introduced into

ScPO₄, the heating pattern showed some variations. Upon heating, first physically and chemically bound water was evaporated from the mixture and NaOH was melted above 300 °C. However, the pyrophosphate formation was not observed as the temperature goes higher. Hence, as an initial observation, conversion of ScPO₄ with the addition of NaOH can be claimed to be successful.

The conversion products were analysed by powder XRD for phase identification. Here in this paper, we present the results from two selected conversion mixtures: ScPO₄ + NaCl and ScPO₄ + NaOH. As shown in Figure 3 (left), the initial ScPO₄ appears to be amorphous with a broad low-intensity peak centred at 2θ = 27°. Since the melting point of NaCl is at 801 °C, observable changes were only evident start from the 750 °C sample. With the treatment at 900 °C, the final phases were identified to be sodium scandium phosphate [Na₃Sc₂(PO₄)₃] and the reacted sodium chloride. The results obtained are not acceptable since scandium is still associated with the phosphate moiety after conversion.

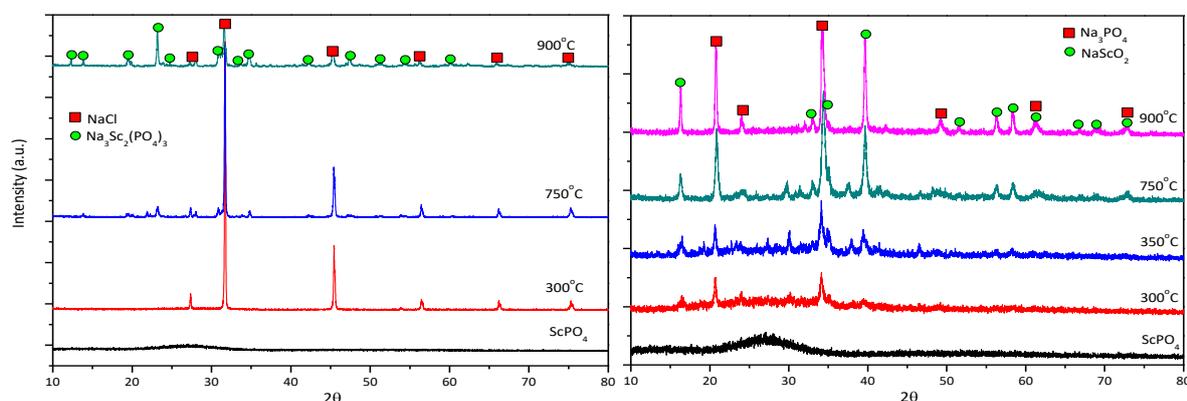


Figure 3. XRD patterns of ScPO₄–NaCl mixture (left) and ScPO₄–NaOH mixture reacted at different temperatures

The situation alters when using NaOH, as illustrated in Figure 3 (right). Note that both NaOH and ScPO₄ are XRD amorphous. The peaks representing sodium phosphate (Na₃PO₄) started to appear already from 300°C, indicating the occurrence of solid-state reactions. The final phases after 900 °C conversion were assigned to sodium phosphate and sodium scandate(III) (NaScO₂). Similarly to aluminium oxide, scandium(III) oxide is amphoteric thus scandium forms oxyanions. The transformation of scandium from cations to anions effectively separates the scandium and phosphate moiety. A simple subsequent water washing step could dissolve all sodium phosphate while leaving the sodium scandate(III) in the solid phase.

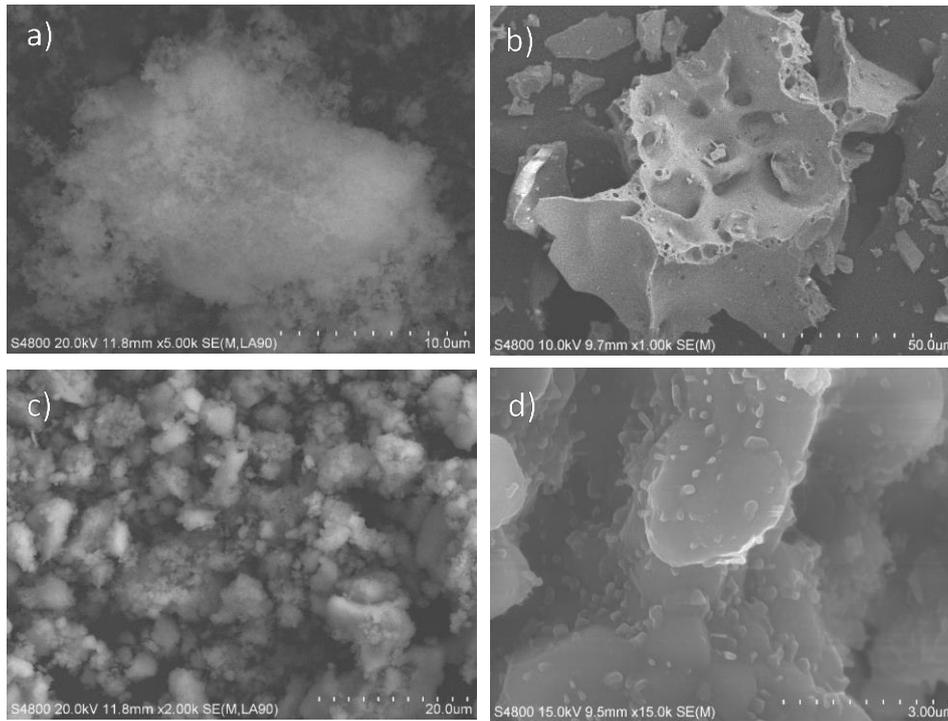


Figure 4. SEM micrographs showing a) synthesised ScPO_4 , b) synthesised ScPO_4 heated up to $900\text{ }^\circ\text{C}$, c) $\text{ScPO}_4 - \text{NaOH}$ mixture at $350\text{ }^\circ\text{C}$ and d) $\text{ScPO}_4 - \text{NaOH}$ mixture at $900\text{ }^\circ\text{C}$

After the verification of the conversion by reacting ScPO_4 with lower melting point sodium compounds in the solid state, the morphology of the particles was investigated. Figure 4 shows SEM micrographs of heat treated and reacted ScPO_4 products. The difference between two different ScPO_4 samples, before and after $900\text{ }^\circ\text{C}$ heat treatment can be seen from Figure 4a and 4b. While ScPO_4 has small particle size initially, as temperature increased, these particles sintered together and produced a porous material. Although not indexed, this phase is likely scandium pyrophosphate.

When reaction with NaOH was initiated in the heating stage, the morphology showed a great difference as it was summarized in Figure 4c and 4d. At $350\text{ }^\circ\text{C}$, it can be seen that small ScPO_4 particles surrounded and stuck to the NaOH melt homogeneously. As it was shown earlier in the XRDs, even at that temperature solid-state reaction of phosphate exchange was initiated at the interfaces, this counts for one reason of this morphology. Further increasing the temperature up to $900\text{ }^\circ\text{C}$ resulted in more homogeneous and almost completed reaction. The two major phases, Na_3PO_4 and NaScO_2 are classified as the rigid body and the tips from the body respectively (Figure 4d). EDS scans showed that Sc concentrated in the tips of the morphology while P diffused towards the body to form Na_3PO_4 .

Conclusions

In this study, synthesized ScPO_4 is tried to be converted into other Sc-compounds and reacting ScPO_4 with NaOH converted it successfully to NaScO_2 . Sodium compounds having high melting point ($>750\text{ }^\circ\text{C}$) showed poor conversion since a more stable ScPO_4 compound, $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ is formed before transformation can occur. Sodium compounds having low melting point ($< 400\text{ }^\circ\text{C}$) showed successful conversion at temperatures even lower than their melting points. Phosphate which removed from ScPO_4 , diffused towards sodium compounds where Na_3PO_4 compound is formed. Obtained scandium phosphate concentrate from the pregnant leach solutions can be further purified by converting it with sodium compounds, since the solubility of different sodium-metal oxides will differ from each other.

Acknowledgements

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