

HYDROMETALLURGICAL EXTRACTION OF SCANDIUM FROM LATERITIC NICKEL ORES

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Abstract

This paper mainly aims to focus on the precipitation behaviour of scandium during the pH controlled solution purification process in the course of hydrometallurgical processing of lateritic nickel-cobalt ores. The experimental findings showed that considerable amount of scandium can be precipitated, concentrated and used as a secondary scandium source in a two-step pH controlled solution purification process of nickel-cobalt production. After obtaining the scandium enriched precipitate, the sulphuric acid leaching experiments showed that 98% of scandium can be extracted into the leach solution and it can further be recovered by solvent extraction or ion exchange method.

Introduction

Scandium being one of the rare earth elements has lack of affinity for the common ore forming anions and rarely concentrated in the Earth's crust. It is generally found in more than 100 minerals in trace amounts, and up to present it has been produced as a by-product during the processing of uranium, tin, iron, tungsten, tantalum, zirconium, titanium and other rare earth elements. Since the main supply of scandium is provided as a by-product of other metals, the annual production is around 5-12 tons having a price of 2000-3000\$ for 1 kg of 99.9% Sc₂O₃ ^[1].

As a result of the fact that there is no abundant, reliable and low cost scandium supply throughout the world, the applications of scandium are confined to mainly three different areas. In the literature; it is stated that the addition of a minute amount of scandium (0.2-0.8%) into aluminium provides excellent enhanced corrosion, mechanical and welding properties^[2]. That's why previously Al-Sc alloys have been used in missiles, fighter jets, aerospace applications and high-tech sporting equipments where the performance is much more important than the cost. If the cost and abundant supply issue is solved, there is a great potential for the use of Al-Sc alloys in vast areas such as; high voltage transmission lines, sporting goods, aerospace and automotive industries. Other than Al-Sc alloys, the use of scandium in

solid oxide fuel cells (SOFC's) as solid electrolytes gives exceptional properties. Sc-doped fuel cells allow lower operation temperatures and provides extended operating life together with highly efficient, low cost green energy production. Finally, the outstanding properties of scandium is exploited in lighting applications. Scandium compounds used in high intensity vapour lamps resembles and replicates the sunlight effectively that's why they are used in stadium lights, TV cameras, film and television industry for good colour-reproduction.

Although; reliable, abundant and low cost scandium production could not be realized up to now, there is a great potential to recover scandium as a by-product from the hydrometallurgical extraction route of lateritic (oxide) nickel-cobalt ores. In a previous work, the high pressure sulphuric acid leaching behaviour of a typical lateritic ore containing 106 g/t scandium was studied and it was found that 80.6% of scandium within the ore could be extracted into the leach solution together with nickel, cobalt and other impurity elements^[3] having the PLS (pregnant leach solution) analysis given in Table 1;

Table 1 Concentration of metals in the PLS and the prepared synthetic solution

| Element | PLS Comp. (mg/L) | Synt. Soln. (mg/L) | Reagent Used |
|-----------|------------------|--------------------|--|
| Nickel | 5502 | 5827 | Ni(II) Sulphate Hexahydrate |
| Cobalt | 321 | 371 | Co(II) Sulphate Heptahydrate |
| Scandium | 34 | 30 | Sc(III) Sulphate Octahydrate |
| Iron | 1688 | 1814 | Fe(III) Sulphate Hydrate |
| Aluminium | 3985 | 4317 | Al(III) Sulphate (18.H ₂ O) |
| Chromium | 342 | 150 | Cr(III) Sulphate Hydrate |
| Manganese | 2110 | 2056 | Mn(II) Sulphate Monohydrate |
| Magnesium | 1285 | 1369 | Mg(II) Sulphate Heptahydrate |
| Copper | 28 | 29 | Co(II) Sulphate Pentahydrate |
| Zinc | 73 | 74 | Zn(II) Sulphate Heptahydrate |

Generally, this type of solutions are processed by MSP (Mixed Sulphide Precipitate) and MHP (Mixed Hydroxide Precipitate) methods in order to recover nickel and cobalt intermediate products. In MSP Method, the solution is directly treated with hydrogen sulphide gas to selectively precipitate mixed nickel-cobalt sulphide product. However; in MHP Method, the pH and temperature of the solution is adjusted to remove impurities and at the end to obtain a mixed nickel-cobalt hydroxide product. In this study, the main aim was to focus on to recover scandium in an MHP Circuit without affecting the conventional production route of the mixed

nickel-cobalt hydroxide product. To understand the process chemistry and predict the behaviour of scandium during temperature and pH controlled MHP Process, Figure 1 was obtained by using the solubility product data of ions at 25 °C^[4, 5].

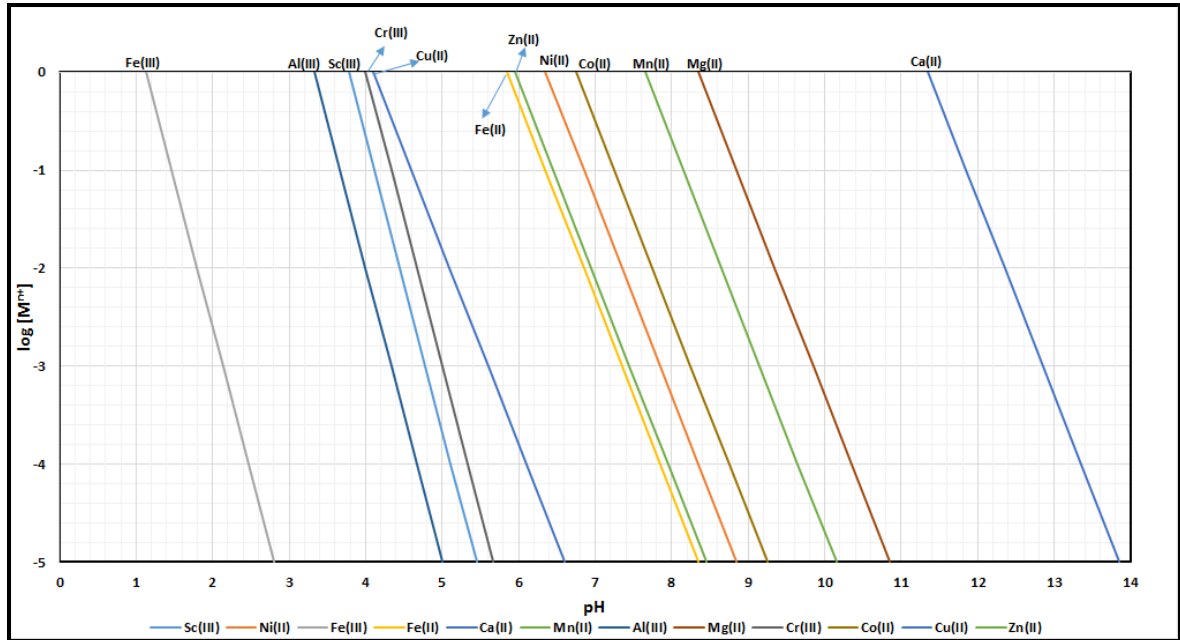


Figure 1 Behaviour of ions w.r.t to molar concentration of ions and pH at 25 °C

According to Figure 1; by considering equal molar concentrations, it is predicted that the cations are going to precipitate with increasing pH in the following order due to hydrolysis reactions in the solution; Fe(III) > Al(III) > Sc(III) > Cr(III) > Cu(II) > Fe(II) > Zn(II) > Ni(II) > Co(II) > Mn(II) > Mg(II) > Ca(II). Depending on the precipitation behaviour with increasing pH; the conventional MHP Process is devised with two impurity removal steps in order to eliminate the co-precipitation and loss of nickel and cobalt together with precipitated impurities^[6]. The first step is generally conducted between 80-95 °C and pH between 2.5-3.0, and most of the Fe(III), and some of the Al(III), Cr(III) are removed under this conditions. In the 2nd impurity removal step, the remaining Fe(III), Al(III) and Cr(III) are removed to minute levels at pH level between 4.5-5.0 at around 60°C, and then nickel-cobalt are co-precipitated from the cleaned solution in the form of mixed-hydroxide product at a higher pH. When the behaviour of scandium is examined from Figure 1, it is predicted that scandium is going to precipitate in the 2nd impurity removal step. Therefore; this study has aimed to investigate the possibility of precipitation and separation of the scandium in the 2nd impurity removal step in order to recover it later without affecting the conventional MHP Circuit.

Experimental

In order to investigate the precipitation behaviour of ions with changing pH, a synthetic solution was prepared by using reagent grade salts of the existing ions according to the data given in Table 1. The solution purification experiments via precipitation were conducted in two steps by using a four-necked glass flask, for condenser, temperature, pH measurement and reagent addition. In the 1st step, the pH of the solution was controlled and stabilized at the target pH and temperature by adding small amounts of CaCO₃ slurry (25 g/100cc water) via a micropipette in order to avoid high local pH regions. At the end of the precipitation experiments, the slurry was filtered via a Buchner funnel and a vacuum pump. The solid remaining in the Buchner funnel was washed with de-ionized water at a suitable pH level to eliminate the possibility of precipitation during washing. Then, the liquid and solid samples were analysed by ICP-OES method for mass balance calculations. According to the optimum pH level selected from the 1st step, a stock solution was obtained by using the initial synthetic solution and conducting a series of solution purification experiments at the pre-determined pH level. Then, this stock solution was used for 2nd impurity removal experiments. The pH of the 2nd step experiments was controlled by adding small amounts of CaCO₃ slurry (12.5 g/100cc water) with the same procedure. All of the scandium was aimed to be precipitated and concentrated in the precipitate with minimum nickel and cobalt co-precipitation. After determining the optimum pH level, a series of precipitation experiments were conducted to obtain a stock of scandium enriched precipitate for scandium re-leaching experiments.

Results and Discussion

1st Impurity Removal Experiments

The main aim of the 1st impurity removal experiments was to obtain maximum iron, and some of aluminium and chromium precipitation with minimum nickel, cobalt and scandium losses. The findings of the 1st impurity removal experiments are given in Figure 2;

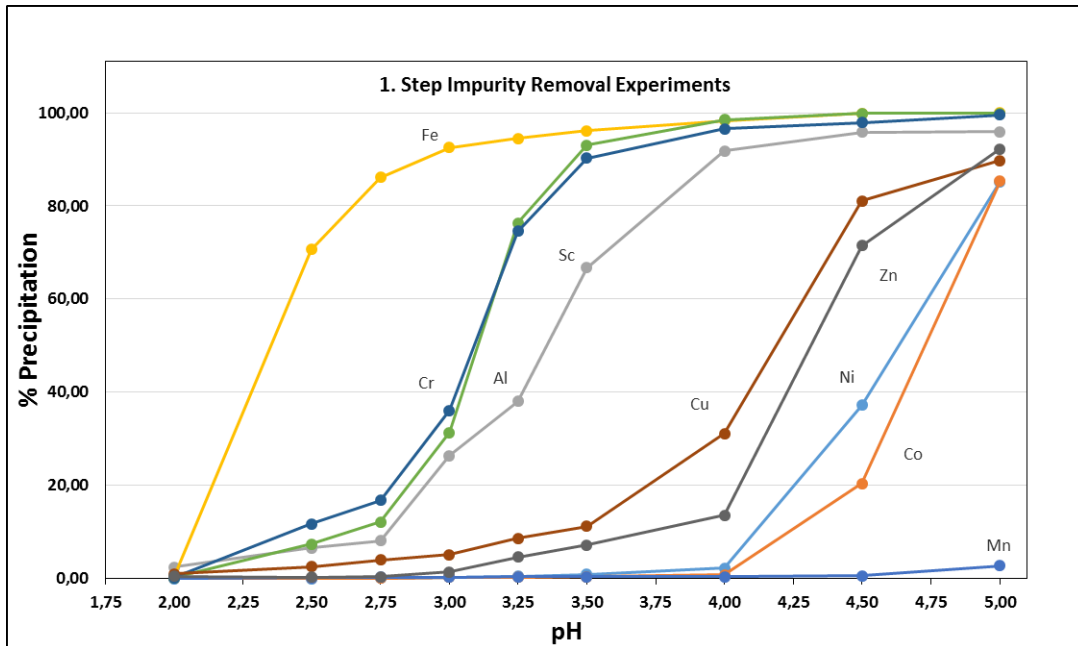


Figure 2 Precipitation behaviour of ions w.r.t pH (90 °C and 120 minutes)

When the results are analysed; it is seen that precipitation of nickel and cobalt became significant after pH 4.00. Since the minimum nickel and cobalt precipitation is desired in the 1st step, pH 4.00 should not be exceeded. In terms of impurity elements; higher pH levels are favourable for the efficient impurity removal. When the scandium is considered, scandium precipitation started to increase after pH 2.75. At pH 2.75 about 8% scandium precipitated, but it increased to about 26% at pH 3.00. Thus, pH should not be increased further in order not to lose scandium in this step. By taking the above mentioned results into consideration, pH of the 1st impurity removal experiments was selected to be as 2.75. In order to provide a stock solution for the 2nd impurity removal step, a series of experiments were conducted at pH 2.75 and the chemical analysis of the stock solution is given in Table 2.

Table 2 Chemical composition of the stock solution after 1st impurity removal step

| Element | Ni | Co | Sc | Fe | Al | Cr | Mn | Mg | Cu | Zn | Ca |
|--------------|------|-----|----|-----|------|----|------|------|----|----|-----|
| Conc. (mg/L) | 4650 | 268 | 23 | 227 | 3599 | 98 | 1905 | 1211 | 28 | 67 | 570 |

2nd Impurity Removal Experiments

The main aim of the 2nd impurity removal step in conventional MHP process is to remove the remaining impurities after the 1st step with minimum nickel and cobalt losses. However, since the aim of this study is to precipitate and separate scandium from the MHP circuit, the maximum scandium precipitation is intended in selecting the suitable pH level. According to Figure 3; it is clear that beyond pH 4.25, it can easily be precipitated and separated from the MHP circuit. In terms of nickel and cobalt, pH should not be increased further than 4.75 due to significant losses of these metals.

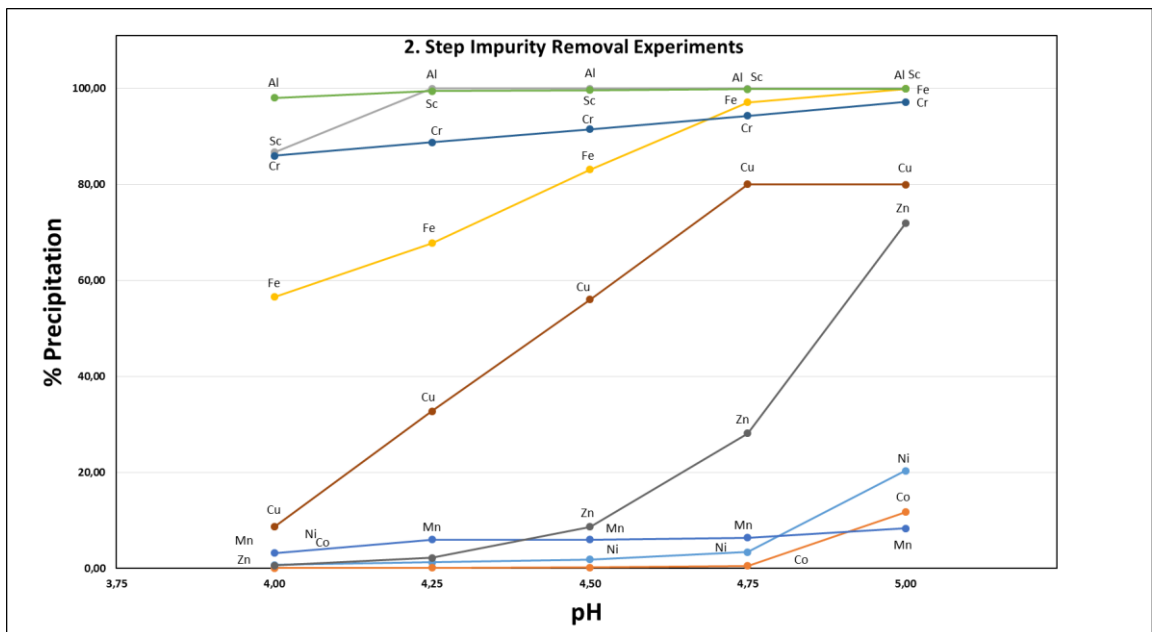


Figure 3 Precipitation behaviour of ions w.r.t pH of the solution (60 °C and 180 minutes)

Therefore; by taking the above mentioned findings into consideration, the selection of pH as 4.75 will be the best choice for the precipitation and separation of scandium from the main production circuit. After choosing the precipitation parameters as 60 °C, 180 minutes and pH 4.75, the resultant compositions of the precipitate and the purified solution are given in Table 3. It is clear from Table 3 that almost all of iron, aluminium and chromium were removed from the solution and initial Sc concentration is upgraded to 703 g/ton as intended.

Table 3 Conc. of the precipitate and the solution after 2nd impurity removal step

| Concentration | Ni | Co | Sc | Fe | Mn | Al | Cr | Cu | Zn | Ca |
|--------------------|------|-----|-----|------|------|-------|------|-----|-----|-------|
| Liquid (mg/L) | 2819 | 241 | - | 2 | 1509 | 4 | <5 | <5 | 41 | 498 |
| Solid ppt. (mg/kg) | 4010 | 36 | 703 | 3100 | 29 | 11.6% | 1446 | 504 | 368 | 14.6% |

Sc Re-leaching Experiments

In order to investigate the extraction behaviour of Sc from this newly formed Sc enriched precipitate, a series of agitation leaching experiments with 0.2 solid to acid-water mixture at 60 °C within 60 minutes were performed. The leaching parameters and the corresponding metal concentrations in the re-leach solution are given in Table 4.

Table 4 Re-leaching parameters and the analysis of the re-leach solution

| Exp. | % Sc Ext. | Ni (mg/L) | Co (mg/L) | Sc (mg/L) | Fe (mg/L) | Al (mg/L) | Cr (mg/L) | Mn (mg/L) | Cu (mg/L) | Zn (mg/L) |
|--|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 25 g/L H ₂ SO ₄ | 42.5 | 373 | 4.6 | 72 | 220 | 8180 | 158 | 3.8 | 50 | 36 |
| 50 g/L H ₂ SO ₄ | 72.5 | 664 | 6.8 | 121 | 507 | 15925 | 344 | 4.4 | 88 | 56 |
| 75 g/L H ₂ SO ₄ | 82.4 | 776 | 7.6 | 136 | 617 | 18683 | 423 | 4.8 | 102 | 65 |
| 100 g/L H ₂ SO ₄ | 91.9 | 928 | 8.7 | 153 | 659 | 18848 | 529 | 4.6 | 102 | 64 |

It is seen from Table 4 that, the concentration of all elements increases with increasing acid concentration. Since the re-leach solution after re-leaching step is going to be further treated for scandium recovery, the aim should be maximum scandium extraction with minimum impurity dissolution. Therefore; considering the considerable increase in the Sc concentration with minor increase in the impurity levels, 100 g/L of H₂SO₄ acid addition seems to be the most suitable acid level. Actually, it seems that further increase in the acid concentration may increase the Sc extraction from 91.9% to higher levels but in order not to increase the acid consumption and the amount of impurity elements, 100 g/L acid seems plausible.

Conclusion

Experimental findings of the selected 1st impurity removal (90 °C, 120 min., pH 2.75) and the 2nd impurity removal experiments (60 °C, 180 min., pH 4.75) showed that after a two-step pH controlled process, scandium can be precipitated and separated from the main MHP circuit with minimum nickel-cobalt losses and effective impurity removal. After the scandium precipitation and concentration, it was found that Sc can be re-leached and taken into the leach solution with 100 g/L of H₂SO₄ acid with 0.2 solid to acid-water mixture at 60 °C within 60 minutes. As a future work, scandium may be recovered from the re-leach solution by solvent extraction or ion exchange method.

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