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Solvent extraction behaviour of scandium from lateritic nickel-cobalt ores using different organic reagents

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Abstract: Scandium is one of the most important and strategic metals that can be recovered as a by-product from lateritic nickel-cobalt ores. In this research, different extractants were investigated to extract scandium from sulphate medium by using solvent extraction method. Generally, the organic extractants are classified as acidic, neutral and basic reagents. Thus, the aim of the present study was to compare scandium extraction efficiencies of some acidic, neutral and basic organic reagents. For this reason, Ionquest 290 (Bis(2,4,4-trimethylpenthyl) phosphonic acid), DEHPA (Di(2-ethylhexyl) phosphoric acid), Cyanex 272 ((Bis(2,4,4-trimethylpentyl) phosphinic acid) which are acidic organophosphorus compounds, Cyanex 923 (Trialkyl phosphine oxide), which is a neutral organophosphorus compound, and Primene JMT, a basic extractant, were used. The extraction efficiencies of these extractants were studied with respect to the extractant concentration at the same pH and O/A (organic/aqueous) phase ratio. As a result of this study, DEHPA and Primene JMT were found to have high scandium extraction efficiencies with lower impurity co-extractions at pH=0.55 with O/A phase ratio 1/1.

Keywords: *Solvent extraction, laterites, scandium, mixed hydroxide precipitate*

1. Introduction

Scandium is a rare earth element and a valuable metal. Although it is widely distributed in the Earth's crust, it generally occurs at low levels. It is mainly substituted for the major elements in minerals such as iron and aluminium, which have three valence electrons similar to scandium. There are only a few scandium ore deposits. Because of this, scandium is generally produced as a by-product during production of other elements, such as titanium, vanadium, uranium, aluminium, nickel, tantalum, niobium, and zirconium and. Scandium is generally enriched in slags, effluents, waste liquors and tailings which form during the processing of these metals (Semenov et al., 1983).

Nowadays, the demand of scandium is increasing due to its use in many application areas. The main applications are high strength and low weight aluminium and magnesium alloys, solid oxide fuel cells (SOFCs), as well as lightning applications, and ceramic lasers. The first and widely spread area of scandium use is in aluminium alloys as an alloying element. Small addition of scandium in aluminium (0.1-0.8 wt-%) improves the mechanical and physical characteristics of the alloy drastically. This provides high strength, low weight, unique precipitation hardening characteristics and high thermal stability to alloyed aluminium parts and these alloys are generally used in aerospace components, military applications, high performance sporting equipment, and some electronic components (Ahmad, 2003; Harata et al., 2008).

The other area of scandium use is in solid oxide fuel cells in which scandium oxide is added into stabilized zirconium oxide as a solid electrolyte to increase the thermal stability, ionic conductivity, and the operating life of the fuel cell. Addition of scandium oxide allows operating at lower temperatures, thus increasing the efficiency of the energy production by decreasing the heat losses

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(Ciacchi et al., 1991*).* Additionally, scandium compounds are used in lightning applications such as high intensity halide lamps and lasers, since it can provide the replication of sun light effectively.

In this study, scandium is extracted and recovered as a by-product from the hydrometallurgical extraction processing of lateritic nickel-cobalt ores. Some lateritic type nickel cobalt ores are processed by using MHP (Mixed Hydroxide Precipitation) method in order to recover nickel and cobalt as hydroxide intermediate product. In MHP method, the control of pH and temperature of the pregnant leach solution (PLS) are important for removal of the impurities from the solution before the precipitation of nickel and cobalt.

The flowsheet given in Fig. 1 is an illustration of a commercially available Ni-Co laterite processing plant operating in Turkey (META Nikel-Kobalt A.Ş.). According to the MHP production circuit (Fig. 1), after the ore preparation, high pressure sulphuric acid leaching (HPAL) is carried out by using autoclave. As a result of the leaching process, the nickel bearing leach solution and leach residue are obtained. While the leach residue is being removed from the system, the separated leach solution passes through two neutralization stages prior to precipitation of the MHP product.

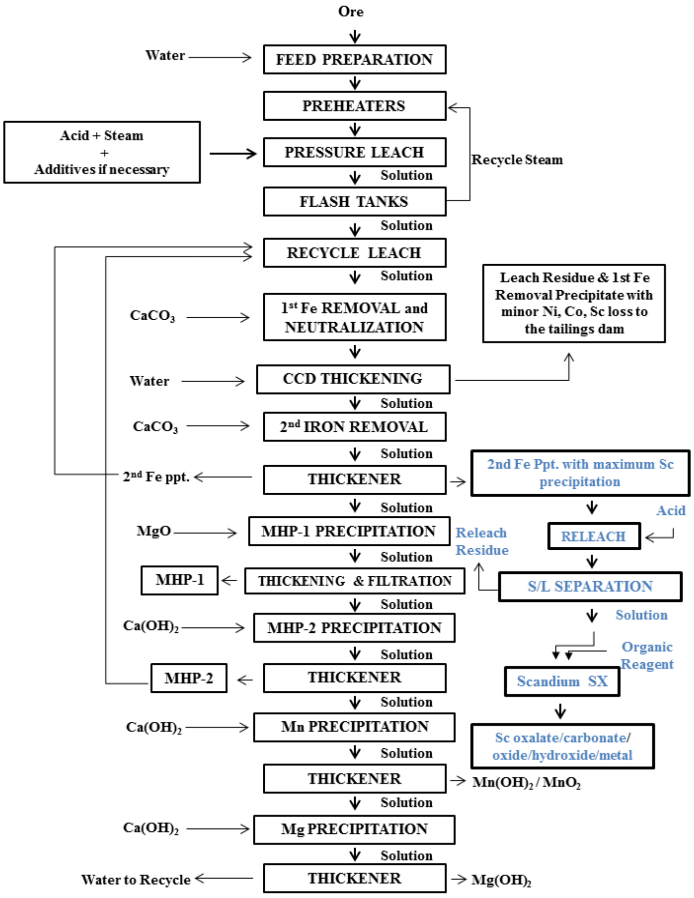

Fig. 1. Mixed hydroxide precipitation (MHP) circuit

On the basis of solubility product data of ions at 25 °C (Fig. 2), the precipitation of cations with increasing pH can be predicted. According to Fig. 2., the precipitation of ions occurs in the following order: Fe(III) > Al(III) > Sc(III) > Cr(III) > Cu(II) > Fe(II) > Zn(II) > Ni(II) > Co(II) > Mn(II) > Mg(II) > Ca(II).

The aim of the 1st impurity removal stage is to obtain the maximum iron, aluminium and chromium precipitation with the minimum nickel, cobalt and scandium losses. The suitable pH is approximately 2.75. The solution obtained in the 1st impurity removal step passes through the 2nd impurity removal stage in order to remove impurities still remaining after the first stage. However, in this study, the main aim of this 2nd stage is to provide maximum scandium precipitation with minimum nickel and cobalt losses because the extraction and recovery processes of scandium start with re-dissolving the precipitate obtained after the 2nd impurity removal stage. Therefore, the pH of this step, which is approximately 4.75, should be adjusted according to the precipitation behaviour of scandium. Since one of the most important factors during solution purification is to remove the impurities at a low cost and with available chemicals close to the operating hydrometallurgical plant, limestone in the form of a slurry was used during these two pH adjustment stages till pH 4.75. After these neutralization steps, the precipitation of nickel and cobalt is carried out by two consecutive pH adjustment stages. Initially, the pH of the solution is raised to about 7.0-7.5 by using MgO in MHP-1 precipitation part in order to obtain Ni-Co mixed hydroxide precipitate. Since the precipitate obtained in MHP-1 step is the main product of the overall operation, MgO is preferred instead of limestone in order not to contaminate the MHP-1 product with calcium sulphate, and pH is selected to be 7.0-7.5 to prevent the co-precipitation of manganese together with nickel and cobalt. After separation of the MHP-1 product, the remaining nickel and cobalt is precipitated with $Ca(OH)_2$ at a pH range of 8.0-9.0 and sent to recycle leach step as shown in Fig. 1. The precipitation of the main product is limited at a closely controlled pH range with low impurity co-precipitation. Finally, the solution remaining after Ni-Co precipitation passes through two further stages of neutralization before being recycled back to the main circuit.

In this study, as a result of two-step pH controlled purification processes, a scandium enriched concentrate was obtained during the MHP production process according to the information given by Kaya et al., 2015. After these precipitation processes, the scandium-containing precipitate was leached with sulfuric acid and considerable amount of scandium was taken into the leach solution, which is called as the "Re-leach" stage. After purification and solid/liquid separation, scandium was extracted and recovered from the purified re-leach solution by solvent extraction method.

In solvent extraction experiments different organic extractants were investigated in order to extract scandium from sulphate media. The organic extractants are classified as acidic, neutral and basic reagents. Thus, the main aim in this research was to compare the scandium extraction efficiencies of the different types of the organic extractants. For this purpose, the acidic organophosphorus compounds; such as, Ionquest 290 (Bis(2,4,4-trimethylpenthyl) phosphonic acid), DEHPA (Di(2-ethylhexyl) phosphoric acid), Cyanex 272 (Bis(2,4,4-trimethylpentyl) phosphinic acid), a neutral organophosphorus compound, Cyanex 923 (Trialkyl phosphine oxide) and a basic extractant, Primene JMT, were used. The extraction efficiencies of these organics were studied with respect to the extractant concentration at the same pH and O/A phase ratio 1/1 (Wang et al., 2011).

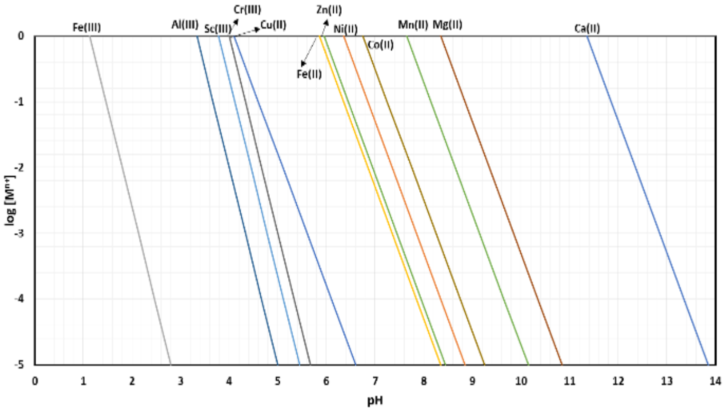

Fig. 2. The solubility product data of ions as hydroxides at 25 °C based on molar concentration of ions (Franzen, 2015)

2. Experimental procedure

2.1 Pregnant leach solution

The analysis of pregnant leach solution used in the extraction experiments is given in Table 1. This solution was obtained after re-leaching of the scandium enriched precipitate which was formed after two neutralization stages during MHP production process. Re-leaching process was performed with 100 g/dm^3 H_2SO_4, 1/5 solid to acid-water mixture ratio at 60 °C for 60 minutes. The obtained solution after re-leaching was purified by using $CaCO_3$ slurry. After the purification and solid/liquid separation, the scandium enriched solution (PLS) was obtained.

Table 1. Composition of PLS (mg/dm^3)

Elements	Al	As	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Sc	Zn
PLS	15549	33	640	294	405	92	2356	328	203	6	5598	46	137

2.2 Test procedures

After the re-leaching and purification processes, the pH of pregnant leach solution was approximately 2.5. Since a higher extraction efficiency and selectivity can be obtained with a lower pH in solvent extraction of scandium, the pH of the PLS was decreased to 0.55 by the addition of H_2SO_4 (Wang et al., 2013).

Each SX experiment was carried out in a 250 cm^3 beaker with magnetic stirring. According to the determination of phase separation rate, all the experiments were performed as aqueous continuous with a phase ratio of O/A = 1/1. To satisfy aqueous continuous phase condition, first the aqueous phase containing Sc was placed to the mixing beaker and mixing was started by the help of a magnetic stirrer to let the continuous phase being the aqueous one which has higher density when compared to the organic phase. Then, the less dense organic phase (organic extractant + diluent) was added slowly to the aqueous phase to maintain the aqueous phase continuity. Moreover, in each experiment, organic–aqueous phase mixtures were stirred for 10 minutes at room temperature (25±1 °C). Then, the loaded organic and aqueous phases were separated from each other by using a separation funnel in order to determine the metal concentrations. The metal analyses after each experiment were done by using inductively coupled plasma optical emission spectrophotometer (ICP-OES).

3. Results and discussion

3.1 Extraction of scandium from sulphate media by DEHPA

Di(2-ethylhexyl) phosphoric acid (DEHPA or HDEHP) is an acidic organophosphorus compound with the formula $(C_8H_{17}O)_2PO_2H$ which is commonly used in the various hydrometallurgical processes, such as the separation and purification of uranium, copper, zinc, cobalt, manganese, and rare earth metals. In this study, iron and aluminium are the main impurity elements in re-leach PLS and they are generally co-extracted with scandium due to their similar cationic properties, i.e. both of them have three valence electrons. Moreover, the nickel and cobalt are also present as important impurities in PLS, as scandium is to be extracted from a precipitate which forms during HPAL processing of lateritic nickel-cobalt ores. Therefore, the iron, aluminium, nickel and cobalt are the impurities which were taken into consideration principally in this study.

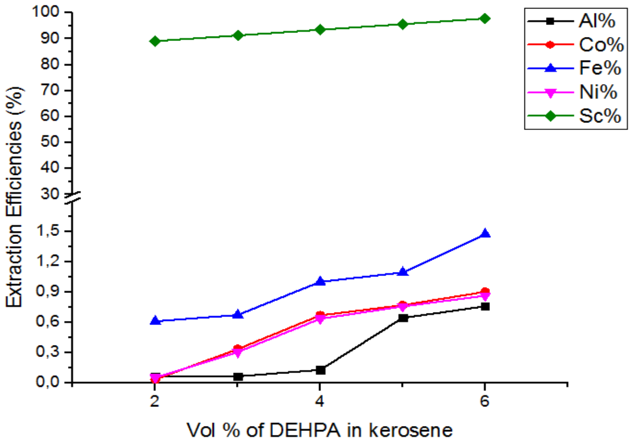

Fig. 3. Extraction efficiencies of Sc, Fe, Co, Ni and Al
with increasing volume percentage of DEHPA in kerosene D60

According to Fig. 3, DEHPA has very high scandium extraction efficiency with low impurity co-extractions. DEHPA co-extracted only limited amounts of iron, aluminium, nickel and cobalt. However, with the increasing volume percentage of DEHPA, more hydrogen ions can be replaced with cations of scandium and the other impurities. In other words, when the volume percentage of DEHPA increases, the amount of co-extracted impurities also increases. Thus, 5 vol-% DEHPA in kerosene D60 can be chosen to be the best condition for scandium extraction of more than 95 % from the pregnant leach solution with acceptable impurity co-extraction.

3.2 Extraction of scandium from sulphate media by Cyanex 272

CYANEX 272 is a phosphinic type acidic extractant which is extensively used in the separation of cobalt from nickel depending on the change of its selectivity according to the pH of the solution. Thus, in this study, the extraction behaviour of scandium from a solution by Cyanex 272 was investigated in order to test its applicability.

According to Fig. 4., although the scandium extraction and co-extraction of other impurities were increasing with the increasing volume percentage of Cyanex 272, only a low amount of scandium could be extracted from the pregnant leach solution. Thus, Cyanex 272 was decided to be an unsuitable organic reagent for scandium extraction for the PLS under investigation.

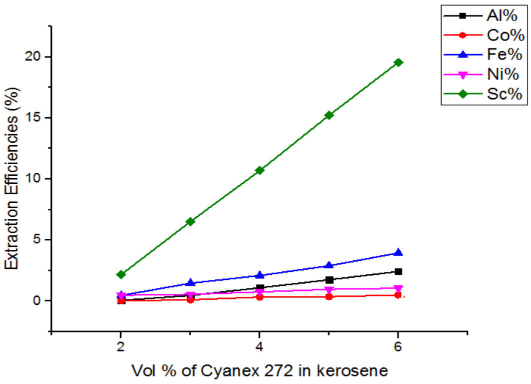

Fig. 4. Extraction efficiencies of Sc, Fe, Co, Ni and Al
with increasing volume percentage of Cyanex 272 in kerosene D60

3.3 Extraction of scandium from sulphate media by Ionquest 290

IONQUEST® 290 is a phosphonic type acidic extractant mainly used in the separation of cobalt from nickel and it can be used in the extraction of other cations such as aluminium, copper, scandium and zinc.

Similar to Cyanex 272, Ionquest 290 has low scandium extraction efficiency. Therefore, Ionquest 290 is also found to be an unsuitable organic reagent to extract scandium from the sulphate media under investigation.

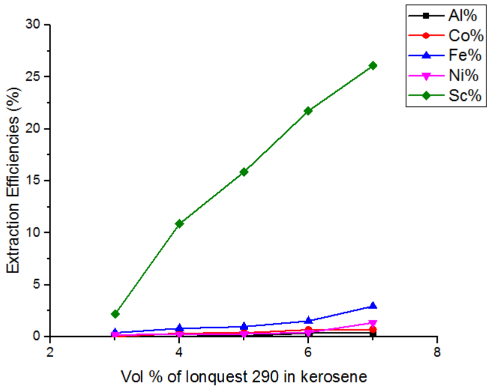

Fig. 5. Extraction efficiencies of Sc, Fe, Co, Ni and Al with increasing volume percentage of Ionquest 290 in kerosene D60

3.4 Extraction of scandium from sulphate media by Cyanex 923

CYANEX 923 extractant is a neutral, liquid phosphine oxide type reagent and mainly used in the recovery of both organic and inorganic solutes from aqueous solutions, e.g. recovery of carboxylic acids from solutions, impurity removal from copper electrolytes, and uranium recovery from phosphoric acid leach solutions.

According to Fig. 6, Cyanex 923 is not a suitable organic reagent for high scandium extraction. Not only scandium extraction is low, but also co-extraction of iron is higher than that of DEHPA. Thus, similar to Cyanex 272 and Ionquest 290, Cyanex 923 was found to be an improper reagent for the extraction of scandium from the pregnant leach solution under investigation.

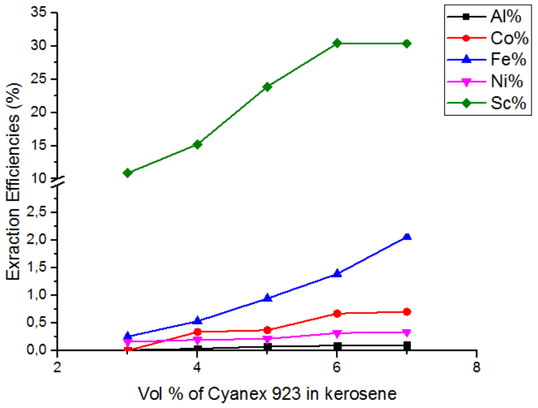

Fig. 6. Extraction efficiencies of Sc, Fe, Co, Ni and Al with increasing volume percentage of Cyanex 923 in kerosene D60

3.5 Extraction of scandium from sulphate media by Primene JMT

Primene JMT is a basic organic extractant, which is a unique member of the family of primary amines. It has special chemical and physical properties such as resistance to oxidation, high fluidity and low viscosity over a wide temperature range. Moreover, it is extensively used in the extraction processes of the rare earth elements. The extraction of metals by amines is considered to depend on the ability of metal ions to form anionic species in the aqueous phase, which are extracted by amines in an anion-exchange process. Since the PLS used in this study is a sulphate based system having a pH of 0.55, enough SO_4^{2-} anions are present in the system to complex with amine extractant according to the reaction mechanism (1) and (2):

$$6RNH_2 + 3H_2SO_4 = 3(RNH_3)_2SO_4 \tag{1}$$

$$2Sc(SO_4)_3^{3-} + 3(RNH_3)_2SO_4 = 2(RNH_3)_3Sc(SO_4)_3 + 3SO_4^{2-}\,. \tag{2}$$

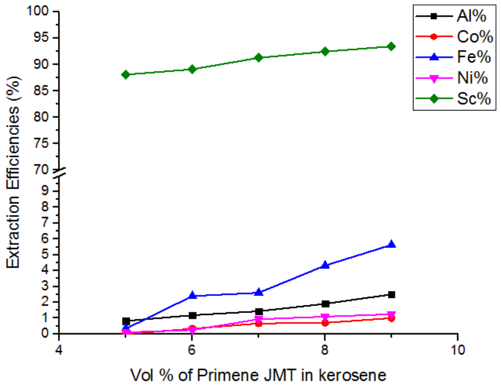

Fig. 7. Extraction efficiencies of Sc, Fe, Co, Ni and Al with increasing volume percentage of Primene JMT in kerosene D60

According to Fig. 7, Primene JMT may be a good extractant for scandium recovery since it has high scandium extraction efficiency with low impurity co-extractions. Although, the scandium extraction increases with the increasing volume percentage of Primene JMT in D60, co-extractions of the other impurities especially iron also increases. Thus, according to the results in order to obtain high scandium extraction with limited impurity co-extractions, 8 vol-% of Primene JMT is the best amount for this extraction process.

3.6 Comparison of scandium extraction efficiencies of different organic reagents

According to Fig. 8, smaller amount of DEHPA is enough to extract scandium in comparison with Primene JMT. In other words, while 8 vol-% Primene JMT is required to extract scandium with limited impurity co-extractions, only 5 vol-% DEHPA is sufficient for the extraction of scandium. In addition, according to Fig. 8, DEHPA has higher scandium extraction efficiency than Primene JMT. Thus, it can be concluded that DEHPA is the best organic extractant for scandium in this study due to high Sc extraction efficiency and low impurity co-extractions. Moreover, DEHPA is cheaper, more widely used, and chemically fairly stable organic extractant. However, the final decision should be done after observing and comparing the behaviour of impurity scrubbing and scandium stripping experiments which will be the topic of a new study.

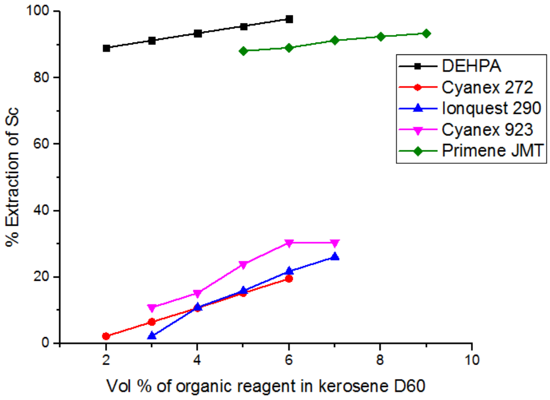

Fig. 8. Extractions of scandium with respect to changing extractant volume diluted in kerosene D60

4. Conclusions

Since acidic environment reported to favour selectivity against impurity elements, pH of the pregnant leach solution was pre-determined as being 0.55. The extraction with 5 vol-% DEHPA diluted in kerosene D60 with a phase ratio of O/A = 1/1 was experimentally determined to give the best extraction efficiency when compared to the other organic extractants. According to the experimental findings, it can be said that DEHPA has the highest extraction efficiency and selectivity for scandium with minimum impurity co-extractions of iron, aluminium, nickel and cobalt. DEHPA can be used effectively for scandium recovery during hydrometallurgical production of nickel and cobalt. Moreover, it is known that DEHPA is fairly stable, relatively cheap, has low aqueous solubility and disengagement from the aqueous phase is considerably fast and complete which makes it practically a suitable extractant for selective scandium recovery from sulphate solutions. Alternatively, Primene JMT was also found to show a good extraction behaviour in terms of scandium with high selectivity towards impurity elements. Therefore, in terms of extraction behaviour DEHPA and Primene JMT are the suitable extractants for scandium extraction from hydrometallurgical nickel and cobalt production circuits. However, final decision should be given after testing the scrubbing and stripping behaviour of these reagents.

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