

# THE SOLUBILITY/DEGRADATION STUDY OF ORGANOPHOSPHORIC ACID EXTRACTANTS IN SULPHURIC ACID MEDIA

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## Abstract

In order to improve the efficiency of the extractant or to prevent the loss of the extractant during metal extraction process the degradation/solubility loss of different organophosphorus acidic extractant was investigated. The effects of acid concentration, extractant concentration, temperature, diluent concentration were examined. Also, the kinetic study at different temperature on extractant degradation/solubility was investigated. Two types of extractant candidates such as Cyanex 272 (bis-2, 4, 4-trimethylpentylphosphinic acid) and D2EHPA (Di-(2-ethylhexyl) phosphoric acid) were tested. Sulphuric acid ( $H_2SO_4$ ) was used in this experiment as an aqueous medium. In this study the pattern or characteristics of extractant solubility /degradation was observed based on organic transfer to the aqueous phase. With regard to phosphorus (P) content in the aqueous phase measured by inductively coupled plasma spectroscopy (ICP) the degradation/ solubility of D2HEPA was more than that of Cyanex 272.

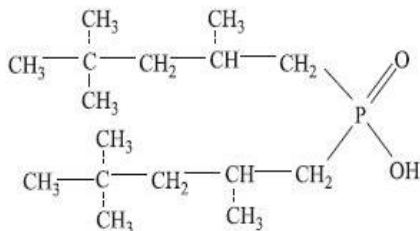
## Keywords

hydrometallurgy; degradation; solubility; cyanex272; D2EHPA

## Introduction

Different types of ligand were used with about 30 toxic Organophosphorus extractants are widely used for the extraction and separation of Ni/Co in hydrometallurgical processes. According to Flett<sup>1</sup> there are more than 40 reagents are on offer for hydrometallurgical use and at least twelve of them are in everyday use.

The extractant, Cyanex 272, is a proprietary but technical grade item of Cytec Canada Inc (CCI). Its active component is bis-2,4,4-trimethylpentylphosphinic acid. Cyanex 272 extractant has proven to be the reagent of choice for the separation of cobalt from nickel from both sulphate and chloride media<sup>2</sup>. The structure of Cyanex 272 is as follows



Di(2-ethylhexyl)phosphoric acid (D2EHPA) has been shown to be an effective extractant and extensively used in hydrometallurgical processes for the separation and purification of divalent transition metals such as copper, cobalt, manganese, and zinc<sup>3</sup>.

The chemical formula of this extractant is  $[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2POOH$ .

There are always some losses of solvent in any solvent extraction process. The economic advantage of a solvent extraction process over other separation process for metals extraction can be lost if the loss of organic solvent from the process become excessive<sup>4</sup>. The replacement/make up of organic solvent in a solvent extraction plant plays a significant role in operating cost. Several factor such as entrainment, solubility evaporation and degradation cause losses in any solvent extraction process and the most significant of them is undoubtedly entrainment. The loss due to degradation particularly encounters the loss of the extractant component<sup>5</sup>.

Not only the cost involved with extractant loss but also there is zero tolerance for organic transfer to electrowinning circuit. If organic transfers in the electrowinning circuit it may clog the anode bag which will reduce the current efficiency<sup>6</sup>. As a result periodic cleaning of anode bag is necessary which is a laborious

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job that also hampers the production operation. So, the solvent loss issue resulting from extractant solubility and/or degradation in this context has become an important issue to select the best solvent extractant.

It is clear that any chemical reaction which destroys the functional group or which creates an antagonistic or negative catalytic impurity constitutes a degradation process. According to Demopolous et al<sup>7</sup>, both physical solubility and chemical stability can be responsible for solvent loss. In order to quantify and characterize organic transfer to aqueous phases and to find out the origins of dissolution and degradation an examination is therefore needed.

In the present work, experiments were carried out to find solubility/degradation losses by showing the effect of different parameters such as acid concentration, extractant concentration, temperature, diluent concentration etc. The kinetic study at different temperatures on extractant degradation /solubility was also investigated.

## Experimental

All experiments were carried out using 25 vol.% extractant diluted in Escaid 110, which is a commercial aliphatic kerosene. 5 vol. % 1- Decanol was used as a phase modifier. Escaid 110 was kindly donated by Univar Canada Ltd and 1 – Decanol was purchased from Alfa Aesar. All aqueous solutions were prepared using reagent grade chemicals.

All tests except kinetic studies were conducted in a programmable air bath shaker (Innova-43 Incubator shaker Series from New Brunswick Scientific) to control the temperature, time and shaking speed of the mixer. Experiments on the kinetic study were carried out in a magnetic stirrer. In each test equal volumes (10 mL) of organic and aqueous phases 0.001M sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) were taken into a 250 mL conical flask and continuously agitated for 1-8 hours to attain equilibrium. The shaking speed and the temperature were maintained at 300 rpm and at 25 °C respectively except those experiments which were done to show the temperature effect. After agitation the solution was transferred into separatory funnels where complete phase separation took place.

To find out any residual phosphorus in the diluent (Escaid 110) or modifier (1-Decanol) the chemicals as supplied by the manufactures were also contacted with fresh 0.001M sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and analyzed by ICP.

For kinetic study on degradation test equal volume (100 mL) of the organic and aqueous phases were taken into a 800 mL Pyrex beaker and the solution was stirred by a magnetic stirrer at 25 °C. The speed of the magnetic stirrer was maintained at 1200 rpm. Samples were taken out using a pipette at 10 minutes, 1 hr, 2 hr, 5 hr and 24 hr time interval. Collected samples were transferred into separatory funnels for complete phase separation.

In all tests, aqueous samples were centrifuged using a centrifuge (Model: 5810 Eppendorf) for 15 minutes at

2000 rpm and analyzed for residual phosphorus concentration by inductively coupled plasma spectroscopy (ICP-MS; Model: Elan DRII). In order to be more accurate phase separatory filter paper (SP1) was also used to remove an entrained organic from the aqueous solution.

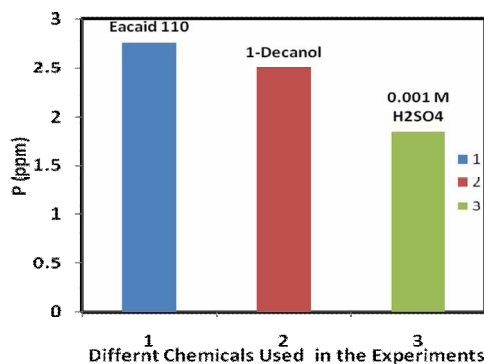
## Results and Discussion

In this work the solubility/degradation of the extractants was determined based on the phosphorus (P) content in the aqueous solutions. In order to confirm whether phosphorus (P) is coming from other reagents like diluent (Escaid 110), modifier (1-Decanol) or aqueous sulphuric acid, tests were conducted and the results are shown in Table 1 and Figure 1.

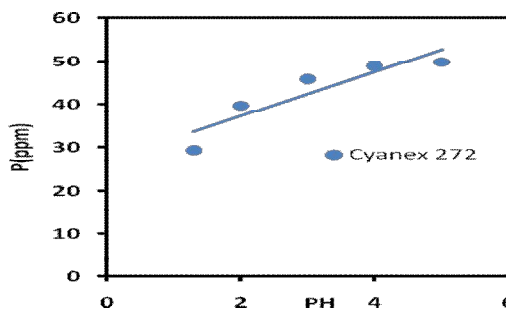
**Table 1. Concentration of Residual P in Different Chemicals Used in the Experiments.**

Chemicals	A/O Ratio	P(ppm) Content
Escaid 110	1	2.76
1-Decanol	1	2.50
0.001 M H <sub>2</sub> SO <sub>4</sub>	-	1.84

From Table 1 and Fig1 it is seen that the amount of phosphorus (P) in the Escaid 110, 1-Decanol, and 0.001M pure sulphuric acid is very low, which acts as a baseline for the further comparison of solubility/degradation of the extractants.



**Fig 1. Initial P Content of different Chemicals Used in the Experiment.**



**Fig 2. Effect of Acid Concentration on Phosphorus**

### Dissolution.

Figure 2 shows the extent of degradation/solubility of Cyanex 272 when exposed to various concentrations of sulphuric acid. From the above figure it is clear that with the increase of sulphuric acid concentration the phosphorus content in the aqueous phase increases, which indicate that Cyanex 272 is soluble at higher pH range. Though the solubility/degradation is high in the range of pH 4 - 5 but considering the true plant condition, for the rest of the experiment pH 3 was chosen

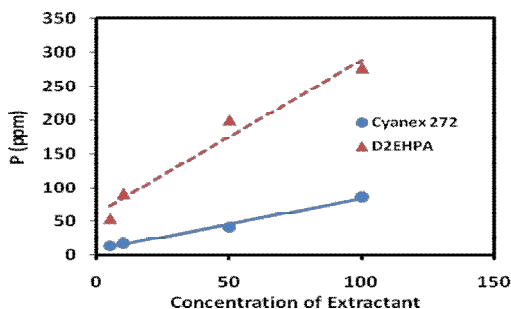


Fig 3. Effect of Extractant Concentration.

In this experiment two organophosphoric acid extractant such as Cyanex 272 and D2EHPA were contacted separately with 0.001M sulphuric acid and the concentration of the extractant was varied from 5 to 100 vol %. It is seen from Figure 3 that both extractants have solubility/degradation in contact with sulphuric acid and the solubility/degradation increases with the increase of the extractant concentration. However, It is clear from Figure 3 that the solubility/degradation of D2EHPA is higher than that of Cyanex 272 at the same experimental condition. In this work 25 vol % extractants were used considering the practical point of view. Kuipa et al<sup>8</sup>, observed that 10-40 vol % of extractant is often optimum in industrial practice

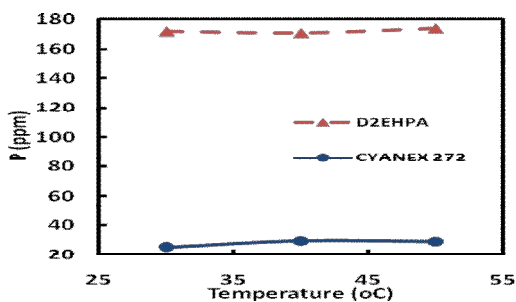


Fig 4 . Effect of Temperature

Figure 4 shows that there is a very little effect of temperature on the solubility of Cyanex 272 and D2EHPA as the concentration of phosphorus in the aqueous solution increases very slightly with the increase in temperature.

Figure 5 shows the kinetics of dissolution of extractant in single contact with sulphuric acid at 25 °C and 50 °C. The above figure shows that the solubility of D2EHPA

increases with time while the solubility of Cyanex 272 remains steady throughout the 24 hr contact with sulphuric acid at 25 °C. However, at 50 °C solubility curve for Cyanex 272 shows an increasing tendency while D2EHPA shows a decreasing tendency. From the kinetic study it is also evident that the solubility/degradation of D2EHPA is more than that of Cyanex 272. At the same conditions, phosphorus level in the aqueous solution for D2EHPA reached at 156 ppm after 24 hr while for Cyanex 272 it was only 32.41 ppm.

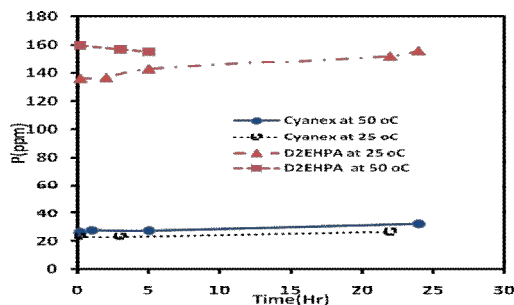


Fig 5. Degradation Kinetics of Cyanex272 and D2EHPA at Different Temperatures.

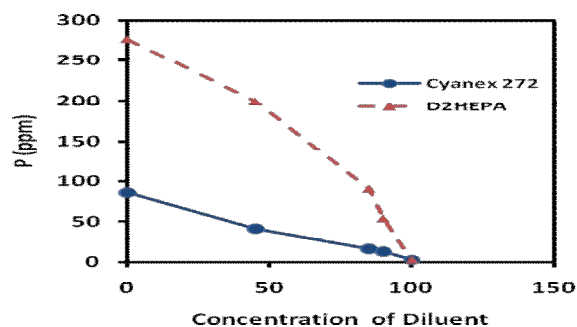


Fig 6. Effect of Diluent Concentration.

Figure 6 shows the extent of degradation/solubility undergone by both Cyanex 272 and D2EHPA when diluent concentration was varied. Here, the diluent percentage was changed from 0 - 100 vol. %. The amount of modifier (5 vol %) was kept constant and the balanced amount was organophosphoric extractant. According to the above curve the solubility/degradation rate decreases with the increase of diluent concentration. In fact it happened as the diluent concentration in the organic phase increases, the extractant concentration decreases i.e. the less concentration of phosphorus in the organic feed. And at 100% of diluent the amount of phosphorus (P) content was only 2.75 ppm which was the baseline phosphorus content.

## Conclusion

The research findings of this work are given below:

- The order of solubility/degradation of Cyanex 272 and D2EHPA tendencies was found to be D2EHPA > Cyanex 272.

- Kinetic study showed that the solubility/degradation of Cyanex 272 was almost same whereas in case of D2EHPA it increases with time.
- With the increase of acid concentration solubility /degradation of both extractant Cyanex 272 or D2EHPA decreases.
- With the increase of extractant concentration solubility/degradation of both extractant increases.
- The solubility/degradation of Cyanex 272 and D2EHPA increases very slowly with the increase in temperature.

The solubility of both Cyanex 272 and D2EHPA decreases with the increase of diluent concentration.

## Acknowledgement

The authors gratefully acknowledge the financial supports from the Vale Inco and the ACOA (Atlantic Canada Opportunity Agency) in the form of AIF grant. In this work Cyanex 272 was kindly donated by the Cytec Canada Inc.

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