

# Extraction of As(V) from sulphuric acid solutions by Cyanex 925

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**Abstract** The extraction of As(V) from sulphuric acid solutions using the phosphine oxide Cyanex 925 dissolved in various diluents was studied. Arsenic extraction depends strongly of temperature, decreasing with the increase of this variable, and to a lesser extent on the sulphuric acid concentration, approximately up to 300 g/L H<sub>2</sub>SO<sub>4</sub>. To increase the degree of arsenic extraction it needs to operate with Cyanex 925 concentrations of at least 50 % v/v, although this also promotes the coextraction of the acid. Stripping of the loaded arsenic and sulphuric acid can be carried out using water, better As-H<sub>2</sub>SO<sub>4</sub> separations can be obtained at lower temperatures or operating using high O/A ratios for acid stripping and lower O/A ratios for arsenic stripping.

Keywords: **Arsenic. Sulphuric acid. Cyanex 925. Solvent extraction.**

## Extracción de As (V) de disoluciones de ácido sulfúrico mediante Cyanex 925

**Resumen** Se estudia la extracción de As(V) de disoluciones sulfúricas mediante Cyanex 925 disuelto en varios diluyentes. La extracción de arsénico depende de la temperatura y disminuye al aumentar esta variable, y también la concentración de ácido sulfúrico, hasta 300 g/L del ácido. Para aumentar la extracción del metal es necesario trabajar con concentraciones de Cyanex 925 superiores a 50 % v/v, aunque a la vez aumenta la coextracción del ácido. La reextracción se puede llevar a cabo con agua, obteniéndose mejores separaciones As-H<sub>2</sub>SO<sub>4</sub> trabajando con temperaturas bajas o con altas relaciones O/A, para reextraer el ácido, y bajas relaciones para el arsénico.

Palabras clave: **Arsénico. Ácido sulfúrico. Cyanex 925. Extracción con disolventes.**

## 1. INTRODUCTION

Solvent extraction has been used in the recovery of copper for nearly 30 years, although the pyrometallurgical process to obtain this metal is still dominant. Thus, a very important part in the production of this metal is carried out by means of the electrolytic refining of copper anodes.

In the electrorefining process some accumulative impurities must be removed from the electrolytes in order to maintain the copper quality and the process efficiency. One of the major impurities present in the electrolytes is arsenic. Some, now considered, conventional processes have been used for the purification of the electrolytes, even considering the potential drawbacks claimed for them.

For a number of years, solvent extraction has been considered as an alternative to the purification of such electrolytes. Several processes and/or extractants have been proposed (1-5).

The objective of the present work is then to obtain information about the characteristics of one of these extractants in the extraction of this element As(V) from sulphuric acid solutions. The extractant used in this work is the commercially available phosphine oxide Cyanex 925 and its performance on extraction-stripping have been evaluated under different variables.

## 2. EXPERIMENTAL

Cyanex 925 was used as obtained from Cytec Ind., the extractant is based mainly in the bis(2,4,4-trimethylpentyl) octylphosphine oxide, being like its related Cyanex 923 a liquid (6). Diluents

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Solvesso 100 and Escaid 100 were obtained from Exxon Chem. Iberia and also were used as received from the manufacturer. All other chemicals were of AR grade.

Extraction and stripping experiments were carried out by mechanical shaking, in thermostatted separatory funnels, of the appropriate aqueous and organic solutions at equal volume phase ratios (unless otherwise stated). After phase disengagement, arsenic was analyzed in the aqueous solution by AAS whereas sulphuric acid loaded in the organic phase was determined by direct titration of the phase with standard NaOH solutions in ethanolic media and using bromothymol blue as indicator. Other concentrations were estimated by material balance.

### 3. RESULTS AND DISCUSSION

Preliminary tests had shown that the extraction of arsenic from sulphuric solutions by Cyanex 925 reaches equilibrium at 5-7 min of contact, independent of the extractant concentration in the organic phase and metal and sulphuric acid concentrations in the aqueous solution. Acid extraction reaches equilibrium even more quickly as there is no variation in H<sub>2</sub>SO<sub>4</sub> extraction in the range of 1 to 40 min of agitation. All extraction equilibrium experiments were carried out within 10 min of contact.

#### 3.1. Extraction

##### 3.1.1. Extraction of As (V) at various sulphuric acid concentrations

Figure 1 shows the relationship between the percentage of arsenic extraction vs the H<sub>2</sub>SO<sub>4</sub> concentration in the feed solution for experiments carried out with an aqueous solution of 1.5 g/L As and organic phases of C925 at various concentrations in different organic diluents and temperatures.

The results can be summarized as:

- the use of an aliphatic diluent (e.g. Escaid 100) is only possible on aqueous solutions with acid concentrations up to 300 g/L; from this concentration up a third phase is formed.
- at equimolar Cyanex 925 concentrations, aromatic diluents present approximately the same efficiency for arsenic extraction than aliphatic ones.
- the increase of temperature decreases the extraction of arsenic.
- to obtain greater arsenic extraction percentages it is necessary to use extractants concentrations of 50 % v/v in the organic phase.

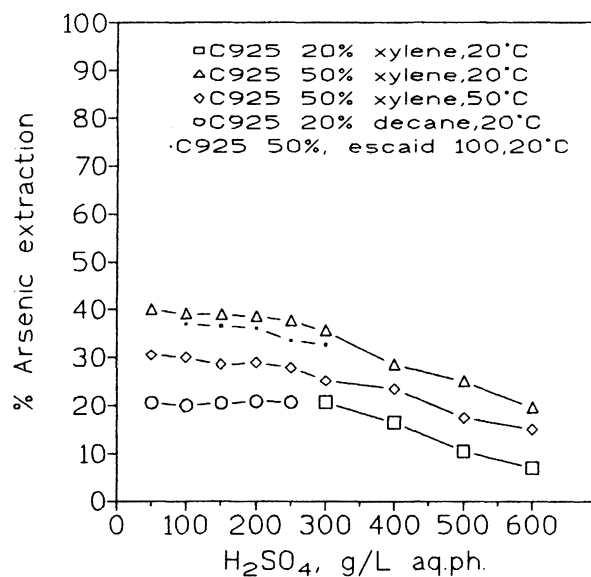


FIG. 1.— Influence of sulphuric acid concentration on arsenic extraction by Cyanex 925.

FIG. 1.— Influencia de la concentración de ácido sulfúrico sobre la extracción de arsénico mediante Cyanex 925.

- sulphuric acid is coextracted with arsenic, the extent of extraction increases with the initial sulphuric acid concentration in the aqueous feed.

##### 3.1.2. Influence of temperature

Although copper electrolytes present elevated temperature due to the electrochemical processes occurring in the electrorefining process and thus will enter at this temperature in the solvent extraction operation, the influence of this variable has been studied in the present extraction system to obtain information about the performance of Cyanex 925 under various operational conditions.

The organic solution was Cyanex 925, 50 % v/v in various diluents, whereas the aqueous phase contained 1.5 g/L As and 200 g/L H<sub>2</sub>SO<sub>4</sub>. The results obtained are shown in figure 2; the extraction of arsenic decreases with the increase of temperature independently of the diluent used in the organic solution. This should be a drawback in the present extraction system; however, the increase of temperature decreases the viscosity of the organic solution which increases with the extraction, especially of H<sub>2</sub>SO<sub>4</sub>.

The coextraction of the acid also decreases with the increase of temperature. Both arsenic and H<sub>2</sub>SO<sub>4</sub> extractions are thus exothermic.

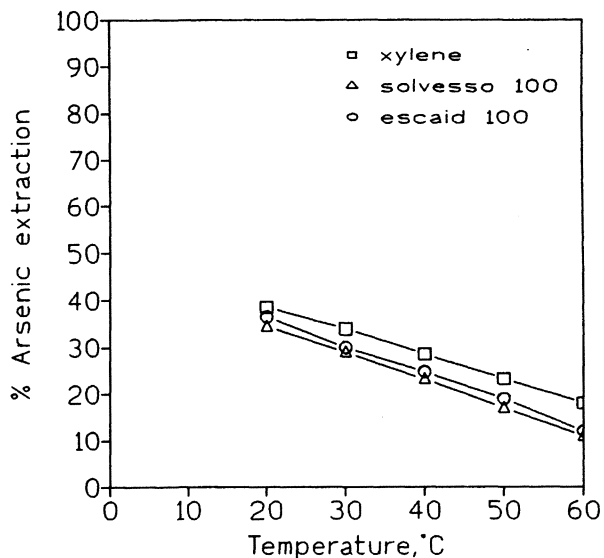


FIG. 2.— Influence of temperature on arsenic extraction.

FIG. 2.— Influencia de la temperatura sobre la extracción de arsénico.

### 3.1.3. Arsenic and $H_2SO_4$ loading isotherms

The loading isotherms were obtained with organic solutions of Cyanex 925, 50 % v/v in Solvesso 100 and aqueous solutions of 6 g/L As and 200 g/L  $H_2SO_4$ , temperature was 50 °C and the isotherms were obtained at various O/A phase ratios.

Figures 3 and 4 show the respective curves for arsenic and sulphuric acid. To obtain better arsenic

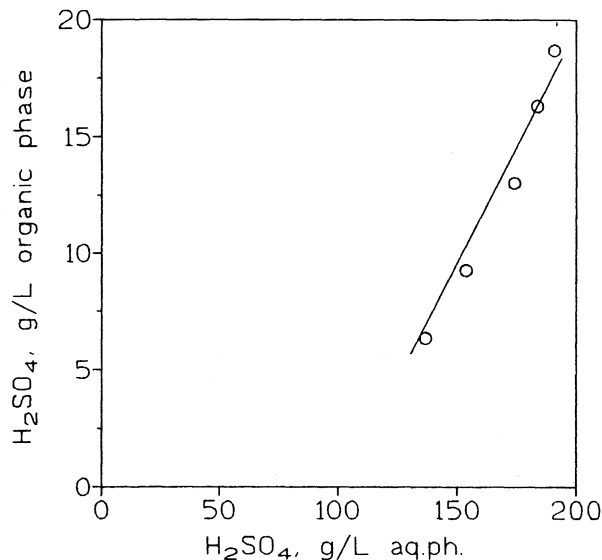


FIG. 4.— Sulphuric acid loading isotherm.

FIG. 4.— Isotherma de extracción de ácido sulfúrico.

loadings it would be needed increasing its concentration in the organic solution. The effect of this increase on arsenic extraction is shown in figure 5 using a solution of 1.5 g/L As and 200 g/L  $H_2SO_4$  and Solvesso 100 as diluent of Cyanex 925. The increase of extractant concentration also promoted the transference of sulphuric acid to the organic solution.

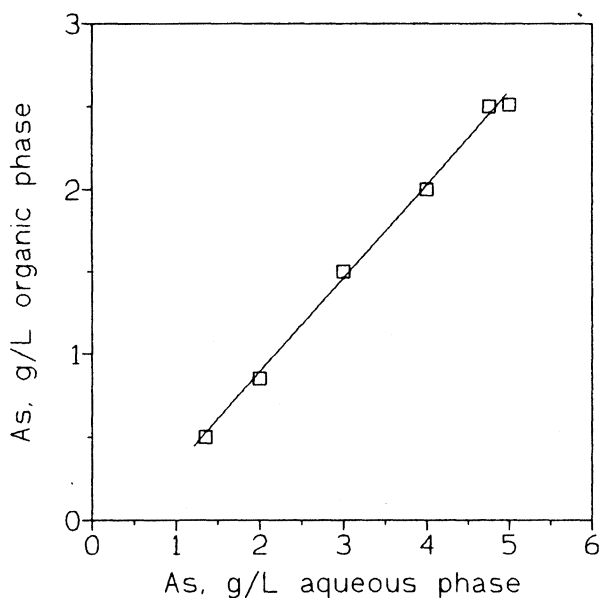


FIG. 3.— Arsenic loading isotherm.

FIG. 3.— Isotherma de extracción de arsénico.

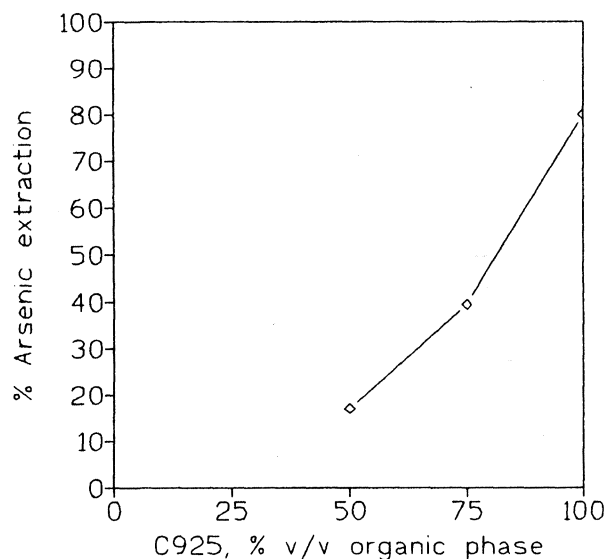


FIG. 5.— Influence of the extractant concentration on arsenic extraction.

FIG. 5.— Influencia de la concentración del agente de extracción sobre la extracción de arsénico.

#### 4. STRIPPING

The stripping of both, arsenic and sulphuric acid, can be accomplished using water. Experiments were carried out using an organic solution of Cyanex 925 50% v/v in solvesso 100 loaded with 1g/L As and 10 g/L H<sub>2</sub>SO<sub>4</sub> and 10 min of contact time. The variables studied were temperature and the O/A phase ratio.

##### 4.1. Influence of temperature

Figure 6 shows the effect of temperature in the stripping of arsenic and sulphuric acid using an O/A phase ratio of 1. In both cases there is an increase in the percentage of stripping with the increase of temperature.

It is evident that better As-H<sub>2</sub>SO<sub>4</sub> separations can be obtained at lower temperatures, although from an operational point of view it should be more convenient to operate at higher temperatures favouring the whole circuit handling.

##### 4.2. Influence of O/A phase ratio. Obtention of the stripping isotherms

Another option to favour the separation of arsenic and sulphuric acid is to operate at different O/A phase ratios. Better As-H<sub>2</sub>SO<sub>4</sub> separations can be

obtained using different O/A phase ratios as it can be seen from the results in figure 7, in all cases temperature was 50 °C. The percentage of sulphuric acid stripping is greater than the corresponding of arsenic at all the O/A ratios; in both cases, the corresponding percentage decreases as the O/A ratio increases.

Thus to obtain better As-H<sub>2</sub>SO<sub>4</sub> separations, the acid should be first stripped at a higher O/A ratio and then arsenic should be recovered at a lower one.

Finally figures 8 and 9 represents stripping isotherms, obtained at 50 °C, for arsenic and sulphuric acid, respectively.

#### 5. CONCLUSIONS

The phosphine oxide Cyanex 925 can be considered as an effective As(V) extractant from sulphuric acid solutions, although it seems to be weaker in this role respect to Cyanex 923. Advantageously, Cyanex 925 extracts less sulphuric acid resulting in relatively higher As-H<sub>2</sub>SO<sub>4</sub> ratios in the first stripped organic solutions. This stripping stage can be carried out very easily using water. Cyanex 925 seems to be a very promising extractant for the recovery of arsenic from copper electrorefining solutions.

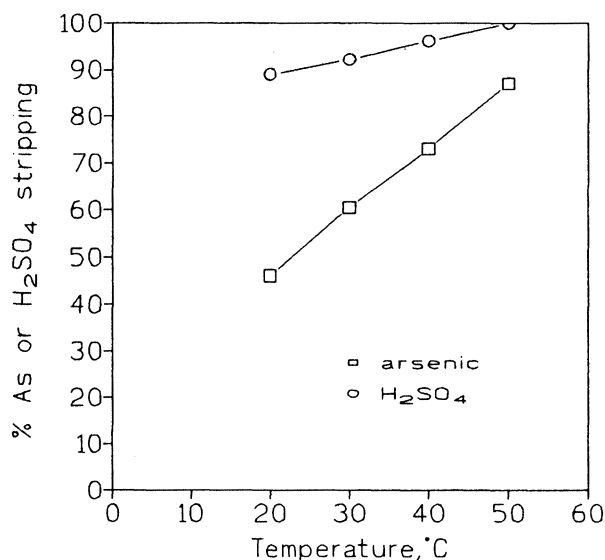


FIG. 6.— Influence of temperature on As-H<sub>2</sub>SO<sub>4</sub> stripping.

FIG. 6.— Influencia de la temperatura sobre la reextracción de As-H<sub>2</sub>SO<sub>4</sub>.

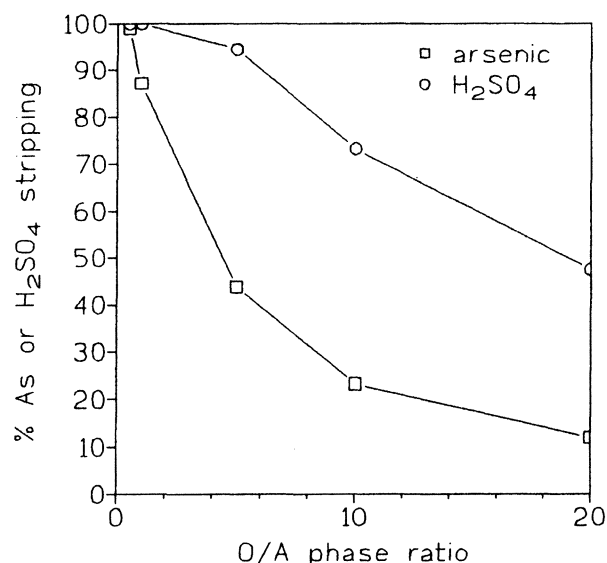


FIG. 7.— Effect of O/A phase ratio on As/H<sub>2</sub>SO<sub>4</sub> stripping.

FIG. 7.— Efecto de la relación de fases O/A sobre la reextracción de As-H<sub>2</sub>SO<sub>4</sub>.

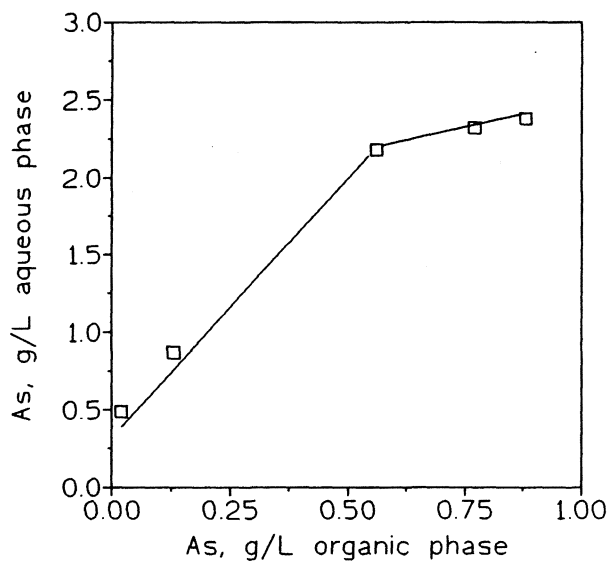


FIG. 8.— Arsenic stripping isotherm.

FIG. 8.— *Isoterma de reextracción de arsénico.*

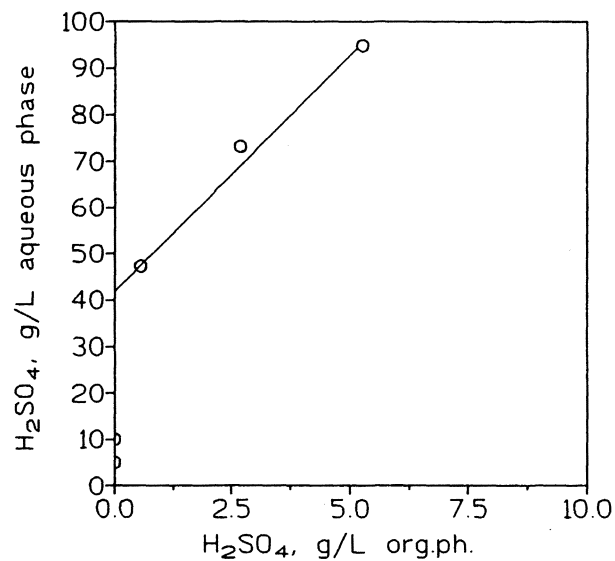


FIG. 9.— Sulphuric acid stripping isotherm.

FIG. 9.— *Isoterma de reextracción de ácido sulfúrico.*

## REFERENCES

- (1) SHIBAYAMA, R. and NAGAI, T. *Solvent Extraction 1990*, T. Sekine (Ed.), Elsevier, Amsterdam, 1992: 1.193-1.198.
- (2) ANONYMOUS. Information on CEPP and LIX 1104. Henkel, 1992.
- (3) DREISINGER, D.B., LEONG, B.J.Y., BALINT, B.J. and BEYAD, M.H. *Solvent Extraction in the Process Industries*, Vol.3. D.H. Logsdail and M.J. Slater (Eds.), Elsevier, London, 1993: 1.271-1.278.
- (4) NAVARRO, P., COEDO, A.G., SIMPSON, J., DORADO, M.T. and ALGUACIL, F.J. *Anais do XVI Encontro Nacional de Tratamento de Minérios e Hidrometalurgia, Vol.II, Metalurgia Extrativa*, A.J.B. Dutra, J.P. Barbosa and R.B.E. Trindade (Eds.), COPPE/UFRJ-CETEM/CNPq-UFF/RJ, Rio de Janeiro, 1995: 177-189.
- (5) WISNIEWSKI, M. *Hydrometallurgy*. 46, 1997: 235-241.
- (6) ANONYMOUS. Cyanex Extractants. Cyanamid, 1991.