

## CONCENTRATION OF HEAVY METALS

### BY PREDISPERSED SOLVENT EXTRACTION

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#### ABSTRACT

This paper discusses a new method to recover and purify solutions containing dissolved metals. The method depends upon dispersion of the solvent prior to contacting the solution to be extracted. In the past, minutely subdividing the solvent has proven impractical because of the slow rate at which minute particles rise by buoyancy. Now it has become feasible to transport small globules of solvent by allowing them to attach to much larger gas bubbles, which rise quickly to the surface and separate cleanly. This technique makes possible the removal of metals down to the parts-per-billion range.

#### BACKGROUND

The disposal of waste has become an exceedingly sensitive and important activity in our high-technology society. Large amounts of environmentally dangerous substances have been made, and sometimes rather carelessly discarded or inadequately stored. Radioactivity in some of these wastes further aggravates the problems of disposing a huge inventories, some decades old.

In solvent extraction it is desirable to create the maximum surface area between the extracting solvent and the pregnant solution containing the solute in order to achieve rapid establishment of equilibrium by facilitating mass transfer of solute across the interface. In conventional solvent extraction this is achieved by vigorous mixing of the aqueous and solvent phases, followed by a settling stage during which the droplets coalesce; or alternatively by breaking up a stream of one phase as it enters the second.

In the new method, named predispersed solvent extraction, (PDSE), only the solvent phase is comminuted, using mainly surface forces, prior to contacting the pregnant aqueous solution. The principle of the method is described in Sebba, see Reference 1. It requires the conversion of the solvent into aphrons,<sup>2</sup> which are micron-sized globules encapsulated in a soapy film which stabilizes them. A concentrate of aphrons containing 90 to 95% oil dispersed in water as the continuous phase is easily made and is known as a polyaphron. When there is a ratio, designated the phase volume ratio or PVR, of about ten parts, by volume, of oil (solvent) to one of water, the polyaphron is very stable and can be stored without deterioration until it is required for use.

In the settling stage of conventional solvent extraction the solvent rises because of its being lighter than water and it then coalesces so that in a short time there are two layers, the solvent floating on the heavier water. If, however, the solvent is used in the aphron form, the separation would be slow because the globules are so minute. For that reason separation is expedited by piggy-back flotation on specially prepared bubbles, which are somewhat larger than aphrons, and are known as colloidal gas aphrons, (CGA). These, as

described in Sebba and Barnett<sup>3</sup>, are 25-50  $\mu\text{m}$  bubbles dispersed to the extent of 60% by volume of gas in water.

Since that paper was written an improved method for generating CGA's has been developed<sup>4</sup> using a rapidly spinning horizontal disc mounted between two vertical baffles. The CGA's are made very quickly in this way and can be pumped and metered into the pregnant solution at any desired rate. They rise reasonably rapidly through the solution, because of their low density, and in so doing they capture the oil globules which adhere to the outside of the bubble shell. On reaching the surface the bubbles burst, the air escapes and the oil remains as a layer on the surface. Because of this procedure it is found that the ratio of solvent to pregnant can be relatively low, as low as 1%. This can sometimes be an important advantage for PDSE.

It should be pointed out that CGA bubbles have three advantages over sparging to buoy up the aphrons. These are:

1. They have an encapsulating soap film to which the aphrons can adhere.
2. They can be metered accurately.
3. They can be delivered at such a rate that there is minimal disturbance of the interface between the water and the solvent layer.

Solvent extraction of metal ions can be used for two main purposes. One is for the recovery of values. In such a case it is usually necessary to choose a solvent system from which the recovered metal ions can be eluted so that the solvent can be reused. In such cases, provided the losses in the process are kept low, the cost of the collector is less important than its efficiency for extraction.

In the second case, solvent extraction can be used for removing unwanted metals from waste streams. In such cases what is most important is to find a solvent that can reduce the concentration of ions in the water to a level that is acceptable to the environmental authorities. As the total quantity of metal that needs to be removed is small, and therefore the amount of solvent needed may be small, the cost of reagents may be unimportant compared to the energy

costs for moving large volumes of water. In the first case a batch process might be satisfactory. In the second case it is almost axiomatic that a continuous process should be used. The new method seems to be particularly appropriate for extraction of heavy metal ions such as uranium and the transuranium ions from dilute aqueous solution.

#### BATCH EXPERIMENTS

This paper will describe the extraction of uranium as the complex uranyl-sulfato ion as this is typical of many of the troublesome heavy metal ions. The solvent chosen was kerosene as this is the one most used in industrial separations. However, for the extraction of uranium a suitable reagent, which can complex with the uranium and make it soluble in the non-aqueous solvent, has to be added to the kerosene. One such reagent examined was alanine, a commercial long chain tertiary amine obtainable from the Henkel Corporation, Minnesota. This is supplied as a solution in kerosene, and for this project it was further diluted tenfold with kerosene. The other extractant was tributyl phosphate, also as a ten percent solution in kerosene.

The method for preparing the aphrons is described in Sebba.<sup>2</sup> It requires a surfactant which is able, without interference from the reagent in the oil, to stabilize the soapy film which encapsulates the oil aphron. On grounds of cheapness and ability to form stable aphrons, a solution containing 5g/L of Arquad 12-50, dodecyltrimethyl ammonium chloride, obtained from Armak Chemicals, in water was used for making cationic aphrons. Ten ml of this was shaken up into a foam in a bottle and 100 ml of a 10% solution of the arquad in kerosene was added in small quantities, with shaking, to form a polyaphron of PVR 10 which was stable enough to be stored. Before use it was diluted fivefold with water.

The method used for making the CGA was that of the spinning disc described in Sebba.<sup>4</sup> The CGA was made in an aqueous solution containing 1g/L of Arquad 12-50.

For this work the pregnant solution was solution of uranium sulfate of concentration varying between  $10^{-1}$  and  $5 \times 10^{-5}$  g/L adjusted with sulfuric acid to pH between 2 and 3, the most suitable for extraction according to the manufacturers of the reagent. For each batch experiment, 2L of pregnant was placed in the cell as shown in Fig. 1.

In order to minimise the possibility of stable foams building up on top of the solution in the cell during the operation, it is desirable that the surfactant used for making the polyaphrons be of opposite charge to the surfactant used in making the CGA. After 2L of pregnant solution had been placed in the extraction cell, a selected quantity of diluted aphrons was introduced into the cell using a Masterflex peristaltic pump. CGA was then pumped into the cell at a steady rate again using a Masterflex peristaltic pump, and after a chosen quantity of CGA had been passed, it was shut off, and after a chosen time interval, the solution in the cell, the raffinate, was analysed for uranium.

The results for the batch tests are shown in Table I. In all cases the volume of the pregnant solution was 2L. The solvent aphrons were introduced into the pregnant solution at the rate of 0.4ml/s followed by CGA in increments of 100 mL at a time, metered in at the same rate. Although in the runs a

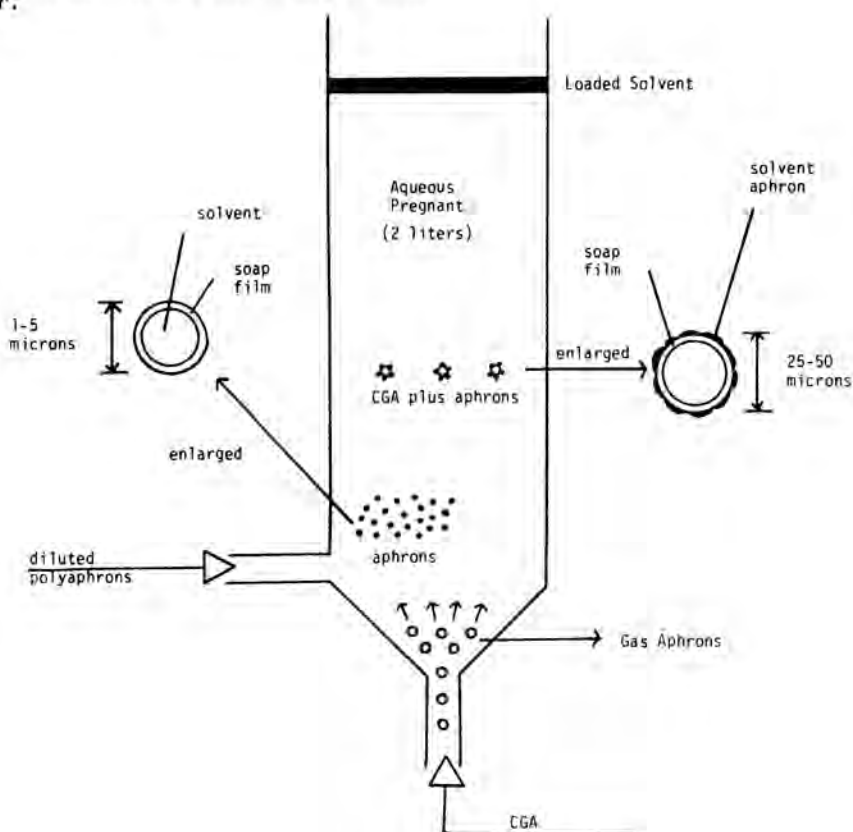


Fig. 1. Predispersed Solvent Extraction.

total of 400 mL of CGA was added to ensure complete extraction, the concentration of remaining uranium was so small as to have reached the limit of accuracy of the analytical method, which is  $1 \times 10^{-4}$  g/L so the % extraction is given after addition of 200mL of CGA. The results listed are the averages of from 8 to 15 separate experiments for each set. The fact that there was not complete extraction at the highest concentrations is believed to be due to the fact that there was not sufficient extraction capacity in the small quantity of solvent which was kept constant for the series of runs.

The fact that virtually complete extraction is possible in one pass emphasises the difference between predispersed solvent extraction and conventional extraction in which the concentrations in both the solvent and aqueous phases are fixed by the necessity to maintain the constancy of the extraction coefficient. In predispersed solvent extraction, because of the enormous numbers of aphrons which move in sequence up the cell, each pass can be considered as made up of an extremely large number of stages and this is responsible for the high efficiency of the process.

#### CONTINUOUS FLOW EXPERIMENTS

A semi-pilot plant unit was designed and built incorporating a glass extraction cell, diameter 12cm and height 55 cm., suitable for either batch or continuous operation. This was tested using copper as the metallic solute. It was mounted on a mobile stand, the objective being not only to have a semi-pilot plant unit which could be used to obtain operating data, but also that it should be sufficiently mobile so that it could be transported to a site for preliminary investigations, in cases where samples could not satisfactorily be sent away for testing purposes. A schematic design of the layout is shown in Fig. 2.

TABLE I

Extraction of Uranium in Batch Cell

Solvent A: Polyaphrons made of 10% Alamine 336 in kerosine. Aqueous phase contains 5g/L of sodium dodecyl benzene sulfonate.  
 Solvent B: Polyaphrons made of 10% tributyl phosphate in kerosine. Aqueous phase contains 5g/L Arquad 12/50. CGA contains 1 mg/L. of sodium dodecyl benzene sulfonate.

Volume of pregnant 2 liters  
 Volume of polyaphrons, PVR 10 50ml  
 Volume of CGA 200ml

Solvent	Initial Conc. g/L	No. of runs	% extraction
A	$1 \times 10^{-1}$	15	90
A	$1 \times 10^{-2}$	15	90
A	$2 \times 10^{-3}$	15	100
A	$1.5 \times 10^{-3}$	15	100
A	$1 \times 10^{-3}$	15	100
A	$5 \times 10^{-4}$	15	100
B	$1 \times 10^{-2}$	8	85
B	$2 \times 10^{-3}$	15	100
B	$1.5 \times 10^{-3}$	15	100
B	$1 \times 10^{-3}$	15	100
B	$5 \times 10^{-4}$	15	100

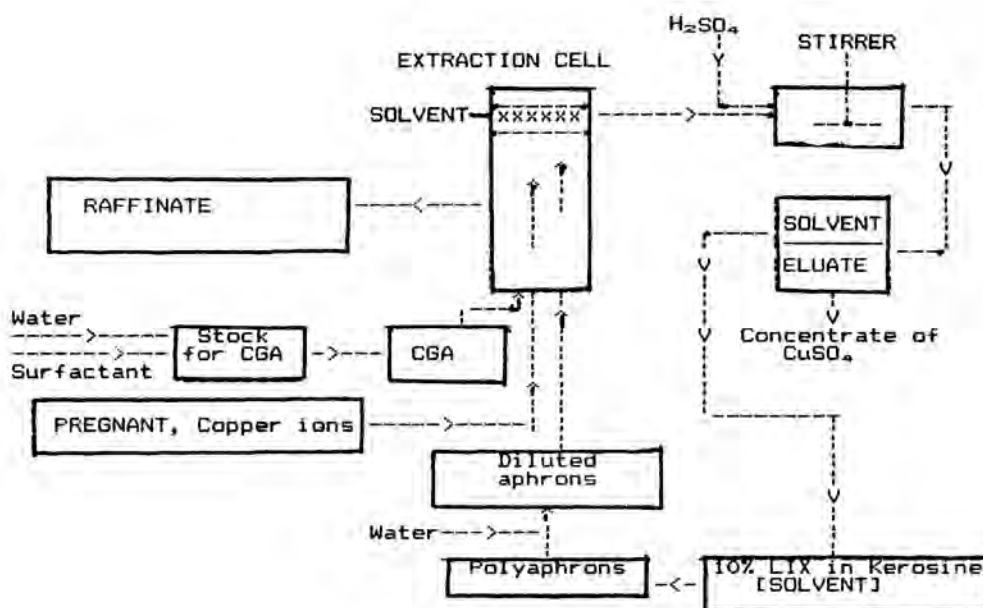


Fig. 2. Flow Plan.

All solutions were pumped from one stage to the next using Masterflex peristaltic pumps. By removing the raffinate at exactly the same rate as the combined incoming rate of the pregnant plus the water included in the CGA, it was possible to control the level of the solvent at a constant level. The equipment functioned extraordinarily well over periods of 8 hours of continuous operation. The first objective was to get some evidence on optimum residence times for the pregnant copper solution. This was achieved by keeping the inflow of pregnant solution, aprons (solvent), and CGA constant and sampling at different heights above the intake point. The results of a few runs are shown in Table II.

It is clear that a certain length of path is required before the extraction becomes efficient. In the above cases it is about 25 cm. It must not be implied from these results that better efficiency could not be obtained under more favourable conditions. The important fact which emerged, but had not previously been demonstrated, is that the path length is important. This will be very relevant if a trough type continuous flow cell is to be designed, as the length of the trough will have to be long enough to ensure that there is a sufficiently long path length.

The solvent layer had a very clearly defined interface with the water, and there was very little foam produced on the top of the solvent. One of the problems being experienced in using conventional solvent extraction in hydrometallurgy is that often a structure appears in the solvent phase. This is referred to as the third phase and is often difficult to handle. Only once in PDSE of copper was such a formation observed and this was very informative. It occurred when there was a break in the flow of CGA enabling breakdown of the CGA bubbles with the consequence that there were large bubbles in the pipeline. It turns out that a thin layer of aprons collects under the solvent layer. These eventually coalesce and merge with the solvent. However, as long as they are in the aqueous phase they remain there as a biliquid foam, as the aprons are so small they do not have enough momentum to penetrate the interface into the solvent layer. But when the large bubbles reach this interface, they have much more energy and so penetrate into the solvent layer, carrying with them some of the biliquid foam. Once inside the solvent layer, the biliquid foam becomes stabilized for reasons that are now understood, and this may be one of the ways by which the third phases are formed. If the presence of large bubbles is avoided this third phase does not appear in PDSE, and

this gives it an important practical advantage over conventional solvent extraction. In 150 extractions of uranium in the batch cell there was not a single case in which the third phase was observed.

In the continuous extraction, the raffinate always showed a turbidity indicating that all the aprons were not reaching the solvent layer, but were being removed before they could do so. As the aprons were not all of uniform size, the smallest ones might not be conveyed to the surface by the CGA. It is possible that if this were to be a problem in an industrial operation, it could be corrected by sending the raffinate to a holding tank before discharge. Another alternative would be to send the raffinate to another cell in which a small amount of aluminum sulfate is added to bring the concentration of aluminum to  $10^{-2}M$ , the pH is adjusted to between 5 and 6 and then a CGA made with 1g/L sodium dodecylbenzenesulfonate is added to float an aluminum soap which carries with it the residual oil. This is really an application of the process of ion flotation.<sup>5</sup> The froth contains all the residual solvent, leaving a crystal clear raffinate with a negligible concentration of copper. However, the loss of solvent in the raffinate may not be such as to justify this procedure. In the runs just reported, the raffinate contained only 0.5mL of solvent/L. As the feed contained 36mL/L of the solvent, this corresponds to a 1.4% loss which, while significant, may not be too serious. In any event these were just preliminary runs and there is every expectation that the performance could be improved as experience is gained.

It was observed that not only did the aprons themselves disperse spontaneously when introduced, but also the CGA's produced adequate mixing. There appeared to be little or no channelling up the walls of the cell.

The experiments have shown that predispersed solvent extraction works very well for the extraction of copper in both a batch and a continuous flow system. The ratio of solvent to pregnant can be very low as compared to what is needed in conventional solvent extraction. The ratio of CGA is also low at about 10%. Further addition of CGA only extracts a minimal additional quantity of solute. As only one third of the CGA is water, this means that the amount of surfactant needed for a liter of pregnant solution is of the order of 300 mg. The quantity of surfactant needed for the aprons is still less, being about 1mg. The smaller the aprons the more efficient is the

TABLE II  
Extraction of Copper in Continuous Cell

Vol of aprons.	Diam of aprons	Charge of apron	Charge of CGA	Cu conc. ( $10^{-6}/L$ )		%Cu Extracted
				Initial	Vol CGA added 100mL 200ml	
10mL	<25 $\mu$ m	anionic	SET 1 cationic	49	3.0 0.45	99.1
15mL	<25 $\mu$ m	anionic	SET 2 cationic	61	0.83 0.43	99.3
50mL	25-50 $\mu$ m	anionic	SET 3 cationic	2200	270 190	91.4
50mL	<25 $\mu$ m	cationic	SET 4 anionic	11900	191 144	98.8
50mL	25-50 $\mu$ m	cationic	SET 5 anionic	2200	277 177	92.0



extraction, but this is offset by the fact that the smaller aphrons take longer to reach the surface. The CGA generator worked satisfactorily over long periods. It would appear that there is enough stirring caused by the introduced CGA to suggest that no further stirring device is needed, but this would need to be verified on a larger scale experiment. The diluted solvent aphrons were stable provided they were kept stirred.

In summary, predispersed solvent extraction (PDSE) represents a new application of surface science to the venerable process of solvent extraction. Properly implemented, PDSE makes possible the removal of metals from aqueous solution down to the parts per billion range.

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