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THE APPLICATION OF MODERN SOLVENT
EXTRACTION TECHNIQUES TO THE REMOVAL
OF TRACE QUANTITIES OF TOXIC SUBSTANCES
FROM INDUSTRIAL EFFLUENTS

W. S. Groenier

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THE APPLICATION OF MODERN SOLVENT EXTRACTION TECHNIQUES
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ABSTRACT

A proposal to fabricate a continuous 4-stage laboratory-scale mixer-settler has resulted from an examination of the engineering aspects of applying solvent extraction techniques to the treatment of industrial effluents. Internal recycle of one liquid phase is featured in each stage to maintain a certain phase ratio, and thereby minimize entrainment losses at the extreme flow ratios that are necessary in this application. The proposed system is to be used to study flowsheet feasibility, to develop operating criteria, and eventually to demonstrate the removal of trace quantities of toxic substances from actual industrial effluents. The system is designed for general application to a wide variety of liquid-liquid extractions but would initially be used to study the removal of mercury from brine solutions by extraction with high-molecular-weight amines.

1. INTRODUCTION

The use of solvent extraction for the recovery of metals has, in the last decade or so, reached a high level of sophistication, particularly in the nuclear industry.^{1,2} In the course of development of this technique, many powerful extractants have been discovered, among which the high-molecular-weight amines are known to have a strong affinity for many metallic anions. It is significant that adjustments of process variables will effect not only the recovery of metals but their separation as well.

In recent years, mercury has been spotlighted as one of the major man-made environmental pollutants. A primary source of this metal is the brine effluent from chloralkali plants. High-molecular-weight amines have been shown to be effective in extracting mercury from brine solutions.^{3,4}

A properly engineered solvent extraction flowsheet will not only allow mercury to be removed, for example, from brine effluents, but will

also permit it to be recovered in a marketable form. In performing these functions, the recovery plant must not add significant amounts of foreign materials (e.g., entrained amines) to the brine. The organic entrainment problem is particularly critical in cases where the solvent extraction plant is operating at a brine-to-solvent flow ratio of, perhaps, 50 or more. Extremely high flow ratios such as this are necessary to allow mercury recovery at high concentration and to produce desirable economic incentives.

The following sections describe a method for minimizing organic entrainment, report on a brief survey of solvent extraction contactor types that are compatible with the described method, and, finally, describe an inexpensive laboratory-scale system for flowsheet study and analysis. The brief survey of contactor types also has application to the choice of contactor for future demonstration and treatment plants.

2. THE MERCURY RECOVERY FLOWSHEET

Solvent extraction techniques are being considered for use in the recovery of many toxic substances, including mercury, cadmium, zinc, cyanide, and other species,⁵ from industrial effluents. Initially, our concern is directed toward a solvent extraction flowsheet for recovering mercury.

High-molecular-weight tertiary and quaternary amines extract mercury essentially quantitatively. The extraction kinetics indicate rapid mass transfer from brine solutions of proper acidity, that is, greater than 99% recovery occurring in less than 15 sec.⁴ Consequently, two ideal stages should suffice for carrying out a liquid-liquid, two-phase, continuous, countercurrent solvent extraction process test. In industrial practice, four to six actual stages, each providing a nominal residence time of about 15 sec, would be desirable.³

Obtaining a high concentration factor for the mercury contaminant is achieved by operation with a high aqueous-to-organic flow ratio in the extracting section and a low aqueous-to-organic flow ratio in the solvent stripping section. Thus 2500 ml of brine could be contacted with 50 ml of organic containing the amine extractant. This mixture,

in turn, could be contacted with 1 ml of strip solution, giving an overall concentration factor of 2500 and a major-phase-to-minor-phase flow ratio of 50 in each contactor during operation. Since mercury contamination in brine effluents is typically at a level of approximately 10 ppm (0.01 g/liter), the strip solution resulting from a process having a concentration factor of 2500 should contain about 25 g of mercury per liter. Concentration factors as high as 10^4 should be attainable.

Several amines have been tested for mercury extraction, and two have been selected for experimental use in this proposal. Alamine 336-S (tricaprylamine), a tertiary amine available from General Mills, Incorporated, Kankakee, Illinois, is suitable for extracting mercury from acidic brine solutions. It can be stripped of mercury by using a basic brine solution. Aliquat 336-S (tricaprylmethylammonium chloride), a quaternary amine chloride also available from General Mills, Incorporated, will extract mercury from acidic or basic brine solutions. Ethylenediamine or propylenediamine (2.5% in each case) is effective as a stripping agent.⁴

A schematic diagram of a flowsheet depicting two ideal extraction and two ideal stripping stages is presented in Fig. 1 for a typical 4.6 M acidic brine solution. The concentration of the amine extractant is shown to be 0.1 M in an inert diluent. Acceptable diluents for amines include xylene and diethylbenzene. Kerosene-type diluents are also acceptable if suitably modified to ensure amine solubility. The use of 3% tridecanol as a modifier in dodecane is recommended.¹

Amine solubilities in water or brine solutions have been measured and are typically less than the 5 ppm detection limit. Removal of amines from effluent brines, in the event that this should become necessary, can be effected by means of a simple inexpensive adsorption unit. The comparatively low toxicity of amines is of little concern at the present time. Of greater importance is the possibility that the brine from a mercury extraction process may be recycled, thus eliminating a large fraction of the total effluent volume.⁵

ORNL DWG 73-3924R1

Fig. 1. Schematic Flowsheet for Mercury Recovery.

The amount of mercury that is extractable in a particular stage depends, to some extent, on the pH of the brine. For tertiary amines, greater than 99% extraction is achieved at a pH of 3 but may be as low as 75% at a pH of 6. Two ideal extraction stages should lower the mercury concentration in brine from 10 ppm to 1 ppb if the pH is such that it allows 99% extraction in each stage, and from 10 ppm to 0.6 ppm if 75% extraction results. The two actual stages proposed for the laboratory-scale mixer-settler system, typically of 95% efficiency, should produce a mercury concentration in the brine effluent of approximately 0.7 ppm at the 75% extraction level, assuming 10 ppm in the starting material. Thus it should be feasible to achieve a mercury removal of at least 93%.

In the testing of other flowsheets yet to be specified for the removal of trace quantities of toxic substances in general, it will be reasonable to assume that 50% of the material is extractable in a single ideal stage. In this case, the two proposed stages, even if operating only at 90% efficiency, should remove 69% of the contaminant from the original feed solution and yield operating data which would be useful in the design of an industrial-scale plant having several stages. Six actual stages operating in the manner just described would remove 97% of the impurity.

3. BATCH DISPERSION COALESCENCE TIME TESTS

A series of batch dispersion coalescence tests was made to determine the practicality of amine-brine flowsheets for industrial use. In these tests, aqueous and organic solutions characteristic of those specified in the flowsheet were vigorously mixed, and the time required for the resulting dispersion to coalesce into well-defined liquid layers was recorded. Measurements were made for various liquid-liquid phase ratios and with both aqueous- and organic-phase-continuous dispersions. A 2-in.-diam turbine having six flat blades of a standardized design was used with a 500-ml tall-form beaker fitted with glass baffles.⁶ Turbine-to-baffle clearance was small in order to create large shearing forces that resulted in very finely divided dispersions. These were

conservative tests since the commercial-scale mixers do not usually produce such finely divided dispersions.

The test results, shown in Figs. 2-5, indicate a practical liquid pair for commercial solvent extraction applications in most instances. For 0.1 M Alamine 336-S in diethylbenzene (DEB) or in 3% tridecanol (TDA)-modified dodecane with 4.6 M brine solutions of pH 1 and 3, dispersion coalescence times were generally less than 2 min. Since the minimization of entrainment is very important in the present application, observations were made of the clarity of the phases in each test and, in instances where cloudiness was very pronounced, samples of the phase were quantitatively analyzed for entrainment. Generally, the organic-phase-continuous dispersions produced the clearest aqueous product phases. Major-phase-to-minor-phase volume ratios in excess of about 4 nearly always led to entrainment. The lower electrolyte content and density of 0.1 M HCl resulted in prohibitively long coalescence times when the aqueous-phase-continuous mode of operation was used.

Similar results were obtained for 0.1 M Aliquat 336-S in DEB or TDA-modified dodecane except that the higher viscosity of this organic compound resulted in longer coalescence times (~3 min) when the organic phase was continuous. Good results were obtained in tests of this compound with brines having pH values of 1, 3, and 9. Again, modest phase ratios are necessary to minimize entrainment. The clearest aqueous products result from organic-continuous operation, but coalescence times in this mode are usually longer than in the aqueous-phase-continuous mode.

Commercial mixers normally exhibit less intensive mixing than that employed in the above tests. However, dispersions showing coalescence times in excess of 300 sec are generally considered impractical for commercial application. For mixer-settler design purposes, the organic-phase-continuous mode was selected for extraction stages. In this mode, a coalescence time of 200 sec is anticipated. For solvent stripping stages, the aqueous-continuous mode was chosen where one would expect a 100-sec coalescence time. Although these choices are conservative for mercury flowsheet mixer-settler design, they are meant to

ORNL DWG 73-3922RI

Fig. 2. Batch Dispersion Break-Time Results for Alamine 336-S in DEB.

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Fig. 3. Batch Dispersion Break-Time Results for Aliquat 336-S in DEB.

Fig. 4. Batch Dispersion Break-Time Results for Alamine 336-S in Dodecane.

provide the flexibility of operation necessary to permit tests of other flowsheets to be made.

4. CHOICE OF CONTACTOR

As seen from the previous section, dispersion major-phase-to-minor-phase volume ratios in excess of about 4 nearly always resulted in entrainment. Since an effective flowsheet will provide a high concentration factor for the recovery of trace quantities of toxic substances from effluents, the flow ratios employed will obviously be as high as practical, certainly in the range of 50 to 100. The solvent extraction contactor chosen for the system should, therefore, feature internal recycle of one of the phases so that the internal phase ratio (major-phase-to-minor-phase ratio) is about 4 or less while the applied flow ratio remains very high. This specification applies especially to contactors that feature fairly intensive mixing.

Initial and operating costs must also be taken into account when a contactor is selected. The most inexpensive contactor types must be given heavy consideration since effluent treatment is usually not viewed as a profitable undertaking but must be supported by other plant operations. Addition of a treatment facility normally results from esthetic or legal pressures. In cases where the recovered materials have a market value sufficient to guarantee a profitable operation, more expensive solvent extraction contactors may be justified.

The chosen contactor must provide a residence time of up to about 15 sec per stage when the phases are mixed intimately to allow mass-transfer equilibrium to be approached, and then contain sufficient space for coalescence, as judged from the coalescence time values in the previous section. Many of the costly contactor types have been developed for specific purposes, such as a short contact time, which may not be compatible with those mentioned above.

4.1 Mixer-Settler Contactors

The simple box-type of mixer-settler contactor probably offers the greatest flexibility of design and operation, and is inexpensive.

Baffled mixers can be sized to provide sufficient contact time, and mixing intensity is adjustable in each stage. The gravity settlers can be arranged to return a portion of the product liquid to the mixer in order to maintain certain phase ratios. Scale-up from laboratory experiments is straightforward.⁷

Flow or in-line mixers that offer little contact time would be usable only if the subsequent settling rate was slow enough to provide the necessary contact time.⁸ The use of coalescence-promoting membranes, screens, or baffles will allow a smaller settling area to be featured and may result in less entrainment for some liquid systems. More efficient phase separation can be obtained by using centrifugal settlers, but at increased cost. The geometrical configuration of the mixer-settler makes this design suitable for portable applications.

4.2 Differential Contact Equipment

Because of the large volumetric flow rates involved in effluent treatment, only mechanically agitated contact equipment can be considered in this category. Towers classified as spray, baffle, packed, or perforated plate would be unreasonably large for most applications. Of the mechanically agitated types, the pulsed, perforated-plate column is probably of foremost importance because of its reliability, cost, and operating characteristics. The intensity of mixing in this unit is generally less than that in mixer-settlers; thus the product may tend to be entrainment-free. The internal phase ratio obtained for a given applied flow ratio is not separately controllable as in a mixer-settler but does vary with the total applied flow.^{9,10} For flow ratios of 50 or higher, with the major phase continuous, phase ratios would be higher than the value of 4 mentioned above; however, the possibilities of low mixing intensity at low pulse frequency--amplitude values may allow the production of very clear product solutions. At a brine-to-solvent flow ratio of 50, for example, the internal phase ratio would be about 24 at flow rates equivalent to 90% of flooding values. If the major phase is dispersed, the internal phase ratio is closer to 2.5. The vertical configuration of this

contactor type may influence its application. Agitation is most effectively applied from a compressed-air pulsed leg. No internal moving parts are required, and the process liquids do not contact the pulsing mechanism.

Other mechanically agitated towers feature internal moving parts but are also of a proven design.⁸ Included among these are the rotating disk contactor; the Mixco (Oldshue-Rushton) contactor, and Scheibel columns. The costs of these systems are probably higher than for a pulsed column because of mechanical complexities.

4.3 Centrifugal Extractors

This category includes the most expensive machines due to the complex design and high rotational speeds developed. They are unsurpassed for use with liquids that tend to emulsify and for the production of crystal-clear product solutions.⁸ Included in this group are the Podbielniak extractor, the Luwesta extractor, the Savannah River centrifugal contactor, and others.^{11,12} A major problem in applying these machines may be the lack of contact time available in such high-speed contactors.

Additional types of solvent extraction equipment are available but do not offer sufficient flow capacity for effluent treatment applications. Since a final product brine having minimum organic entrainment is desired, a final clarifier unit may be specified. Such a device would take the form of a large gravity settling tank with internal coalescence promoters or a continuously fed and discharged centrifuge.¹³

5. CONTACTOR DESIGN

5.1 Laboratory-Scale System

A small mixer-settler system has been designed for laboratory use in testing various effluent treatment flowsheets. It would initially find application in studies of the removal of mercury from brine solutions, as noted previously. The system features two extraction stages,

having 800-ml baffled-glass mixers with 3.4-cm-diam flat-bladed turbines and glass settlers offering a coalescence area of 900 cm^2 . Two stripping stages having 40-ml mixers with 1.3-cm-diam flat-bladed turbines and 45-cm^2 settlers are also featured. Positive-displacement gear or bellows pumps are included to meter flows between stages and to deliver the recycle flows within individual stages. Plastic tubing is specified for hookup. A final deentrainer tank is included. To minimize solution inventories, provision is made to combine purified effluent and mercury-rich strip solution (or other additive solution) in a blend tank for reuse as feed solution.

The system is designed conservatively for the Alamine-DEB--brine flowsheet and is expected to exhibit a concentration factor of 2500 or more. Estimated fabrication costs including pump purchases and overhead are \$1000 per stage.

The proposed system would require preloading of the stripping section stages with mercury to allow steady-state operation to be achieved in a reasonable time period. Estimated phase volumes and times required to reach steady state from a barren state are 23 liters and 28 min for brine feed, 7 liters and 6.9 hr for organic, and 2 liters and 106 hr for strip solution. Solvent losses are estimated at 0.5 ml/min, based on 0.01% entrainment loss and a 0.01% vaporization and leakage loss. These values are highly speculative, and their correction would constitute one major objective of the test. A schematic diagram of the equipment is shown in Fig. 6. Phase ratios (major-phase-to-minor-phase) are selected to be about 4 in extraction stages and 1 in stripping stages. Detailed component designs are complete and ready for fabrication.

5.2 System for 100-gpm Effluent Brine

Very rough estimates of equipment size have been made for a 100-gpm stream of brine effluent based on the considerations underlying the design of the laboratory system. For simple mixer-settlers, four extraction stages would each feature 31-gal mixers and 210-ft^2 settlers. Four stripping stages would be much smaller, each having 1-gal mixers

Fig. 6. Bench-Scale Mixer-Settler System for High Flow Ratio.

and 3-ft² settlers. For pulsed, perforated-plate columns, extraction would require a 36-in.-diam column and stripping would require a 5.5-in.-diam column, each having an active height of about 12 ft if a 3-ft stage height is assumed. These columns would operate with the major phase dispersed, with a pulse height and frequency of 1 in. and 30 to 50 cpm, respectively, and would use perforated plates having a free area of at least 20%.

6. RECOMMENDATIONS

It is recommended that the proposed laboratory-scale mixer-settler system be fabricated and used to test flowsheets for mercury recovery from brine, particularly with regard to entrainment and other solvent losses. It is further recommended that a complete solvent cycle be operated to test the feasibility of obtaining a concentration factor at least as high as 2500. Process costs and operating criteria should be obtained for use in process design studies.

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