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CSA Continuous Countercurrent Ion Exchange (CCIX) Technology

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ABSTRACT

The CSA-CCIX concept started at ORNL in 1951. It has been adapted to a wide variety of applications worldwide, in water and waste water treatment, fertilizers, hydrometallurgy, and general chemical processing. Unique features and how it works are described. Two extreme applications are described in detail. One is for the extraction of trace amounts of uranium from a copper leach, at $37.85 m^3/min$ (10,000 gpm) where very high throughput rates are emphasized. The other is for Acid Retardation, where a strong acid waste is purified and recovered. The feed processing rate here is much lower than the resin rate.

INTRODUCTION

The CSA-CCIX system historically started at ORNL in 1951 and was first reported in ORNL-1310(1). There has been continual development and application since that time. This CCIX system is adaptable to a wide variety of applications that push the limits of throughput rate, solution density, and extremes of flow ratios of solution-to-resin. The purpose of this paper is to point out these unique features and describe how the system works.

Two examples are chosen that illustrate these physical extremes. One is the extraction of uranium that occurs in trace amounts in a standard sulfate leach of low grade copper ore tailings. In this case the feed-to-resin flow ratio is about 500. Emphasis is placed on maximized throughput rate, right up to a practical limit of pressure drop. The objective is to minimize equipment size or cost. Even then the equipment is very large due to the enormous volumes and very low levels of uranium.

The other example application, called "Acid Retardation", demands operation in a very dense solution where the feed-to-resin flow ratio is sometimes as low as 0.2(2). Acid Retardation is an example of an ion exchange system that must be run in a continuous countercurrent flow system to be practical. The efficiency increases with solution strength. The higher the acid concentration the lower the solution-to-resin flow ratio. Because of special features of the CSA-CCIX system, these flow ratios are tolerated or handled. An attractive feature inherent with Acid Retardation is that water is the only consumed reagent. Several examples will be given of acid-salt separations.

CSA CONTINUOUS COUNTERCURRENT ION EXCHANGE (CCIX) FEATURES AND HOW IT WORKS

Continuous Countercurrent Ion Exchange (CCIX) is an advanced technology for ion exchange. This technology involves some forty-four U.S. and worldwide patents. The systems consist of a packed bed of resin contained in a closed loop made up of reacting sections. The resin moves in one direction while the liquid moves in another direction (Countercurrent). The ion exchange resin is continuously reacted and regenerated, thus minimizing the amount of resin required for a given amount of liquid to process.

This technology is a great improvement over fixed-bed systems which do not efficiently react the resin, have high regenerant cost, fluctuating effluent quality, large batch waste disposal, and high water consumption. CCIX offers large economic savings, is adaptable to a wide range of waste streams, and has high capacity. For these reasons, CCIX has gained in favor as a practical and valuable process for industrial, municipal, utility, and research applications.

Advantageous Features of the CSA CCIX Unit.

Over the years, there have been several different types of continuous ion exchange equipment. Based on similar features, these may be divided into a few groups. Most of these have come and gone over the last thirty years. The CSA CCIX system claims to be unique and have all the following attractive features. In comparing this CCIX system with other ion exchange systems, the following points may be used for guidelines.

Maximum liquid production rate per unit size equipment. The reason for this is that the resin is retained in the sections with no danger of fluidization. All solutions enter and exit the unit via well screen which will not allow resin to pass. Other than ion exchange kinetics, the only limitation on production rate is pumping pressure drop. This variable is controlled by choosing resin bed depth and resin particle size. In addition, pressure drops in this moving bed are generally lower than in conventional fixed-beds because the top filtration layer is continually broken up when it reaches the backwash section.

Resin is retained as a packed bed. This means that resin beads are adjacent, or as close as they can be together. This also keeps the bed from fluidizing. Each resin bead retains its position relative to all other beads. This allows minimum engineering stage height (Htu), or the maximum amount of ion exchange work per unit size equipment. The contrast in equipment size is very striking in comparison to fluidized-bed type continuous units.

Processing and maintenance of strong solutions. The CCIX system excels in this area because the full ion exchange cycle is carried out in a single loop. Just as much importance is assigned to water rinse and water displacement areas as loading and stripping sections. Dilution and tailing streams are avoided. This emphasis on the handling of water is increasingly important when processing strong solutions where one solution volume exhausts the ion exchange capacity utilization in less than one volume of resin.

In order to squeeze these solution concentrations to a maximum, it is important to maintain sharp interfaces between reacting solutions. This is readily achieved by obeying solution density rules. Almost always, low density liquids are allowed to float on top of high density ones. It should also be noted that solutions may be processed that would normally float the resin if the packed bed of resin was not confined.

A resin pumping system that is accurately controlled and highly variable in rate. By contrast, many other systems depend on the free fall of resin through processing liquid by the force of gravity. This is an enormous limiting factor on production rate or the density of solutions to be processed. In the CCIX system, the resin rate is accurately controlled over a wide range of very fast and very slow rates. It is not uncommon to have solution-to-resin flow ratios of 100 to 1000. It is just as common for the flow ratio to be 0.5. No mechancial or operating burden is imposed by going through this tremendous variation. This feature is of great significance and explains why this particular device is applicable to such a wide variety of problems.

Handling of slurries. One of the distinctive advantages of ion exchange over solvent extraction or reverse osmosis is that unfiltered or unclarified solutions may be processed. Other types of continuous units with fluidized beds have claimed to be better slurry handlers. A standard packed bed of resin is, in fact, like a sand bed filter. However, the packed bed in the CCIX unit does not act as a filter because its filtration tendency is continually broken up. The backwash section continually flushes out foreign matter and resin fines.

It is important that there be a pre-screening unit operation to remove a few types of larger particles, flakes, or fibers which may be present. Finely divided particles which are characterized as being filtered with difficulty, pass through the packed ion exchange bed with ease.

The only special added feature of a slurry handling contactor is to avoid stagnant pockets and provide extra flush out capability.

A prime target for slurry handling CCIX operation is the slimes from phosphate fertilizer operation. The slime particles are very small and the volume of this waste is enormous. From one-third to one-half of the known phosphate and uranium values are contained in these slimes.

How the CSA System Works

Operation. Continuous Countercurrent Ion Exchange consists of a packed bed of resin contained in a closed loop made up of reacting sections which are separated by valves built into the loop (any type of valve which will shear the resin bed such as ball valves, plug-cock valves, or butterfly valves). The resin is moved around the loop in one direction while the solutions brought into the loop through screens (referred to as distributors and having a mesh opening of smaller size than the resin beads) flow countercurrent to the flow of the resin for a predetermined length of time. During this time, the ion exchange reaction takes place and the waste and product solutions are removed from the column through another set of screens called collectors.

Figure 1 shows the general configuration of the system. Any number of reaction sections can be built into the loop depending on the flowsheet requirements. These normally include a loading section, a regeneration section, a regenerant-rinse section, and a water elimination section.

In this system, the counterflow of resin and solution is accomplished by alternately, (1) pulsing an incremental amount of resin while the solution flows are stopped, and then (2) locking the resin in the respective sections while the solution flows are resumed countercurrent to the previous flow of resin.

Step-wise the contactor cycles as follows:

1. During the solution pumping period, which may last for 2 to 10 minutes, Valves B, C, and D are closed and A is open. These butterfly valves isolate the various ion exchange sections. The resin bed is stationary while the solutions are flowing through the sections.

2. Just before the resin movement period, which lasts for about 5 to 10 seconds, the valve between the upper and lower reser-

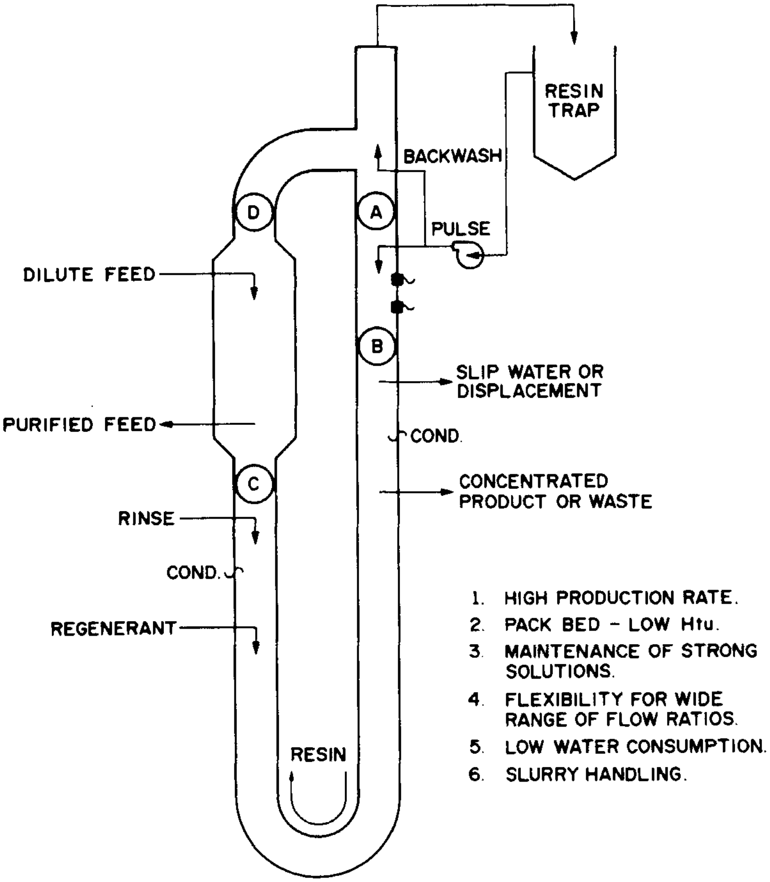

Figure 1. CSA CCIX Contactor - How it Works and Attractive Features.

voirs, "A", closes and the other valves "B", "C", and "D" open. The solution flows are stopped. A hydraulic pulse is applied which slides the entire resin bed a few inches as if it were a piston.

3. When this pulsing phase is complete, the valves are again reversed and the resin locked in the reacting section to be contacted by the solutions. The valve between the upper and lower reservoirs, "A", is open to allow displaced resin to drop into the lower reservoir ready for another cycle.

From the point of view of maintaining interface positions and solution concentrations, the rinse and water elimination sections are most important to understand. During resin movement, the liquids move faster and farther than the resin -- usually two to three times. This movement of liquid by the resin is referred to as slippage.

Thus, the interfaces between the various solutions move around into other sections and it becomes necessary to return them to their original position. This is accomplished in the rinse sections where a countercurrent water rinse makes a void volume displacement of the solution. The rinsing operation is controlled by a conductivity instrument which stops the rinsing action when the interface crosses a probe built into the section.

Also, during the resin pulse, water and resin are moved into the loading and regeneration sections. To avoid mixing this water with the products, a conductivity probe senses the salt-water interface and allows this slippage volume to be separately eliminated before drawing off undiluted product. This is accomplished in the contactor by opening the valve in the elimination port, and keeping the product valve closed until the interface moves past the product port and is sensed by the conductivity probe. The valves are then reversed and strong product is again removed.

EXTRACTION OF URANIUM FROM COPPER LEACH BY CCIX

It is common practice in "open pit" mining of copper to separate ore into "high" and "low" grades. High grade goes through floatation, then to the smelter. Low grade is heaped up in piles called "dumps" and leached with waste sulfuric acid. At some mines all the ore is leached, and there seems to be a trend in this direction.

This leach solution is contacted with scrap iron, in the form of "tin" cans, to drop out finely divided copper metal, called "cement".

$$Cu^{++} + Fe^{o} \longrightarrow Fe^{++} + Cu^{o}$$

There is an increasing trend to replace the use of scrap iron by solvent extraction (SX), or ion exchange (IX), followed by electrowinning. As may be expected, about one-half the metals in the Periodic Table may be found in this leach. Uranium is one of them, at levels of 3 to 20 ppm.

The extraction of uranium from sulfate leach using strong base type ion exchange resin is so well known that this background does not need further discussion. In the late 1950's, 80% of the uranium produced in the world utilized this technology.

This tiny quantity of 5 ppm U_3O_8 hardly seems worth going after. But the leach is already in existence. No mining or grinding is necessary. Millions of gallons are handled anyway for copper. The US Bureau of Mines first explored this source of uranium(3).

Because of the very tiny levels of uranium, at 5 ppm, a paramount demand of ion exchange, or any other step, is that it be fast reacting and high throughput in order to minimize equipment size. This high throughput feature was the over-riding reason for consideration of the CSA-type CCIX system.

At this point the features of this particular CCIX unit will be explained. See Figure 2.

a) Resin fills the loops as a "packed-bed". Since the resin is retained by a screen there is no limitation on flow rate except pressure drop. Since the resin is confined, it cannot float. Therefore, there is no physical limitation on solution density. As a packed bed all resin particles are as close together as they can get, and always stay in the same relative position to each other. This means that stage height (Htu) is at a minimum or the maximum amount of ion exchange work is done per unit size equipment.

b) There is precise control of all flow rates, including the resin. Of equal importance, these flow rates, or flow ratios of resin and solution, may be varied over a very wide range with no loss in precision. This allows this particular CCIX device to be applied to a very wide range of ion exchange applications, Based on field pilot CCIX studies the Feed-to-Resin flow ratio ranges from 500/1 to 750/1 and the 15% H_2SO_4 ratio to resin ranged from 2.5/1 to 3/1.

c) Because of a confined packed-bed, solutions may be kept strong. Water consumption for rinses may be kept as low as a void volume displacement because of the inherent efficiency of continuous countercurrent flow. With this minimum consumption of water, strong processing solutions may be introduced without dilution. The 15% H_2SO_4 strip solution entered and left the CCIX unit without dilution.

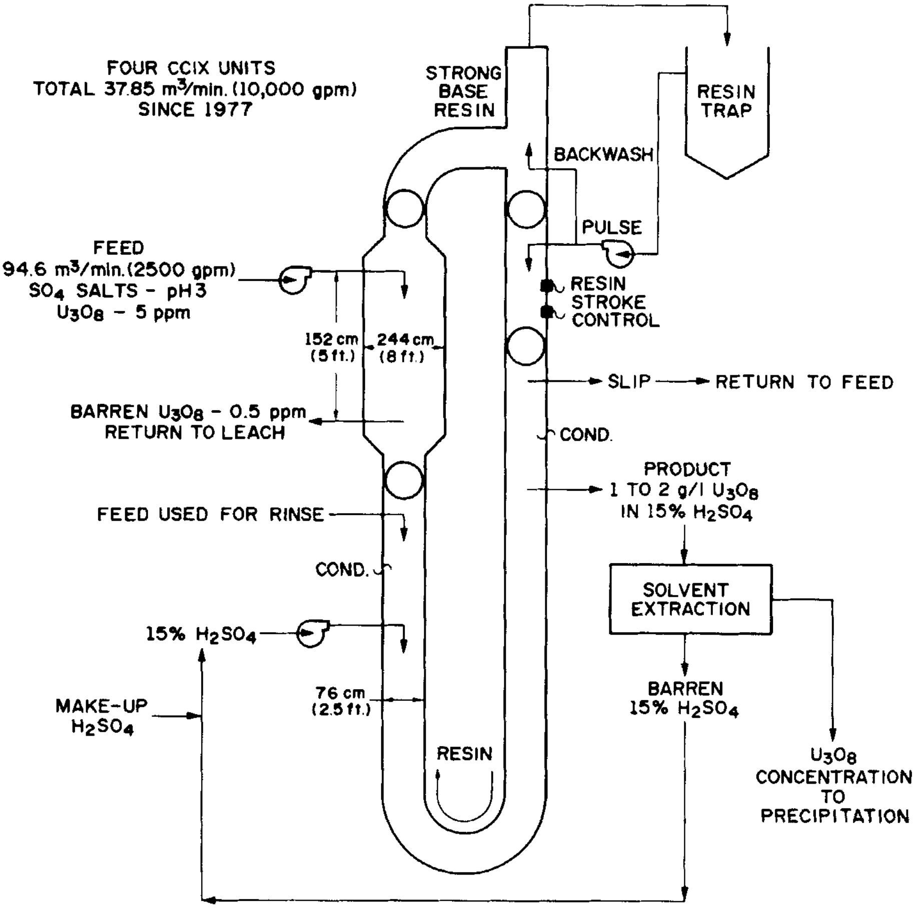

Figure 2. Extraction of Uranium from Copper Leach at Bingham Canyon, Utah.

d) Slurries may be processed without plugging. A packed-bed of resin beads might normally be considered a filter. Because the resin bed is frequently moved, this filtration tendency never gets established.

In the mid 50's, the pulp or slurry handling features of the CSA-CCIX system were demonstrated(4). This was expected to be the "foot-in-the-door" for getting into the mining business. It turned out that the "high throughput" feature was more significant. Anytime there are large volumes, trace components, high distribution coefficient, and fast kinetics, it is most important to process solutions just as fast as possible in order to minimize equipment size. The extraction of this trace amount of uranium, 5 ppm, from this copper leach fits this situation. Even then the equipment must be large to handle large liquid volumes.

When studies were first started on this system, it was surmized that the kinetics of exchange of the large uranyl sulfate anion complex might be the controlling factor, and the equipment would have to be sized accordingly. This time Mother Nature was with us and the exchange rate was found to be very fast. This means that the limiting design factor was pressure drop. A design guideline used is 203ml/min/cm^2 (50 gpm/ft^2) at about 138 to 207 Kilo-Pascals (20-30 psi) per 1.2 to 1.5 meters (4 to 5 foot) depth of bed. This gives a liquid contact time of about 20 seconds and was adequate for >90% uranium extraction. For emphasis it is mentioned again, that very high liquid throughput is a factor of outstanding significance. An 8-foot diameter load section handles 9.46m^3/min (2500 gpm). The Kennecott plant at Bingham Canyon, Utah handles 132.5m^3/min (35,000 gpm) of copper leach, which would require 14 of the 8-ft diameter CCIX units to handle the entire flow. This puts in perspective how important this high throughput feature is.

Pilot testing was done at 4 different sites; 3 heap leaching and one vat. Uranium levels varied from 3 to 20 ppm. From this type leach the distribution coefficient (D.C.) was about 500 to 1000 for strong base type resin. This is a very positive extraction, but it means that the resin loads only to 3 to 5 g/l. From a standard sulfate ore leach one might expect a feed of 500 to 1000 ppm and a resin loading of 70 to 100 g/l. With a low resin loading it is important to use a recycle, or a very economical strip solution. The strip solution used was 15% H_2SO_4. Uranium was extracted and concentrated by solvent extraction with recycle of the H_2SO_4 ion exchange strip solution.

Uranyl sulfate has a much greater affinity than ferric sulfate, but the unused resin capacity was occupied by ferric ion. This low resin capacity utilization for uranium was caused by the low feed level, 5 ppm, and the limiting D.C. of 1000 in pH 3 Sulfate solution. In the fresh leach, jarosite, KFe-III $(SO_4)_2$, was at the saturation level. When the solution hit the enriched ferric ion on the resin in the loading section, then jarosite crystals formed and finally plugged the bed. Therefore, feed to the CCIX was used "after" the contact with scrap iron. The jarosite plugging problem was eliminated because the bulk of the iron was ferrous instead of ferric.

The purpose of the scrap iron was to reduce cupric ion to copper metal, but some hexavalent uranyl ion was reduced to quadrivalent uranous ion. It was discovered that the uranous sulfate anion complex had about 2/3 as much affinity for the resin as the uranyl sulfate anion complex. With this lower D.C., uranium losses were prevented by lowering the Feed-to-Resin flow ratio from 1000/1 to 500/1. Each of the leach sites were different. Where there was no danger of jarosite formation, fresh feed was used to avoid the problem of lower resin affinity of U-IV as compared to U-VI.

The plant installation was made at the Kennecott site in Bingham Canyon, Utah. Four 2.44 meter (8-ft) diameter load section CCIX units were installed to handle 37.85m^3/min (10,000 gpm). This is about one-third of the 189,300m^3/day (50 X 10^6 gpd), which is processed for copper. The first unit was started in 1977 and the other 3 added successively as built. On this writing, the plant is still operating on a 4 to 5 ppm U_3O_8 feed. It is interesting that there are only two fluids in the system; feed and 15% H_2SO_4. Feed is used for resin pulsing, backwash, and strip rinse.

There is greater than 90% extraction when using fresh resin. After a few months, the resin is gradually poisoned, (by silica, grease, gypsum, hydrated oxides, or whatever), and the extraction drops to about 80%. It is a kinetic problem because the extraction will increase by lowering the feed rate. An especially tough anion resin is used, and the resin life is about 1 1/2 to 2 years. Attempts to clear up the resin have not increased the kinetics, so there is no strong incentive to extend the resin life. This is a type of resin attrition caused by irreversible poisoning, not mechanical break-up or resin capacity loss.

This same copper leach contains 30 ppm each of nickel and cobalt. The Bureau of mines at Salt Lake City has measured a distribution coefficient (D.C.) of about 50 for these 2 metals for Dow Chemical Company's new copper selective resin, XFS-4195(5). A few flowsheet and equipment changes need to be made, but here is another opportunity to recover valuable metals without mining or gringing.

While discussing the extraction of trace metals from copper leach, it should not be overlooked that a pilot study was made at Inspiration, Arizona for the production of 16Kg/day (35 lbs per day) of wire grade copper from a similar copper leach by the CSA-CCIX unit and electrowinning(6).

ACID PURIFICATION AND RECOVERY BY ACID RETARDATION USING CCIX

The hardest things to describe are those that are extremely simple. This is a problem with "Acid Retardation". The actual mechanism is not really fully understood by the experts in the field (2).

Acid Retardation is a method for selectively extracting strongly dissociated acids from concentrated solutions (Typically 2N to 5N) using strong-base type anion exchange resins. There is no acid sorption from dilute solutions, therefore, by definition, water is the acid elution agent. This simplicity, with water being the only consumed chemical, is a paramount economic factor inherent to the Acid Retardation system.

For practicality, Continuous Countercurrent Ion Exchange (CCIX), is uniquely necessary. The stronger the acid, the greater the resin capacity utilization. The stronger the acid, the lower the ratio of solution-to-resin flow. Subsequently, the lower the solution-to-resin flow ratio, the greater the demand for the inherent efficiency of continuous countercurrent flow. With CCIX equipment, it is common to have a salt and acid product effluent each of no greater volume than the feed. Flow ratios of solution-to-resin typically range from 0.2/1 to 0.5/1. This is quite unthinkable in conventional fixed-bed equipment. The reason that there are not many references to Acid Retardation is because of impracticality with conventional equipment.

Another unique feature using CCIX equipment is the ability to reflux. This means that the sorbed acid may be eluted at increased strength up to the concentration of the salt plus acid concentration of the feed. A concentration of 0.4M HCl to 2.0M has been demonstrated in our laboratory (i.e., not only without dilution, but with a concentration factor of 5).

Acid Retardation is a general purpose treatment method with the most wide spread utilization expected for salt-acid industrial wastes. Not only is alkali saved for neutralization, but acid is recovered for reuse. Problems studied have been anodizing wastes, ion exchange regenerant wastes, metal treating baths, and purification and recovery of lead battery wastes. A comparison of the efficiency of Acid Retardation of the various acids will be given.

Since we have tied Acid Retardation to CCIX operation it will be described in this context. See Figure 3.

As already indicated, feed strengths are usually in the range of 2N to 5N although not tightly limited to this. Only highly ionized acids are considered, or common HCl, HNO_3, or H_2SO_4. The higher the acid strength, the higher the capacity utilization. See Figure 4. The ion exchange capacity of strong-base type resin is usually about 1.2 eq/l. Acid Retardation capacity is not limited to

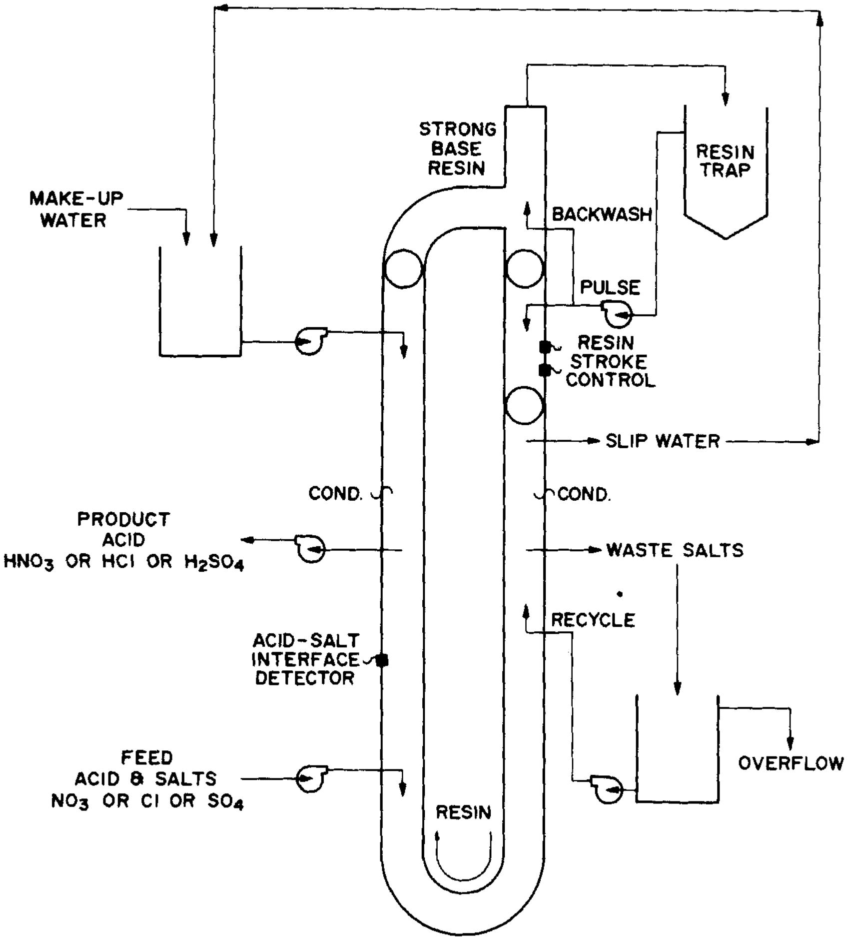

Figure 3. Acid Retardation by CCIX

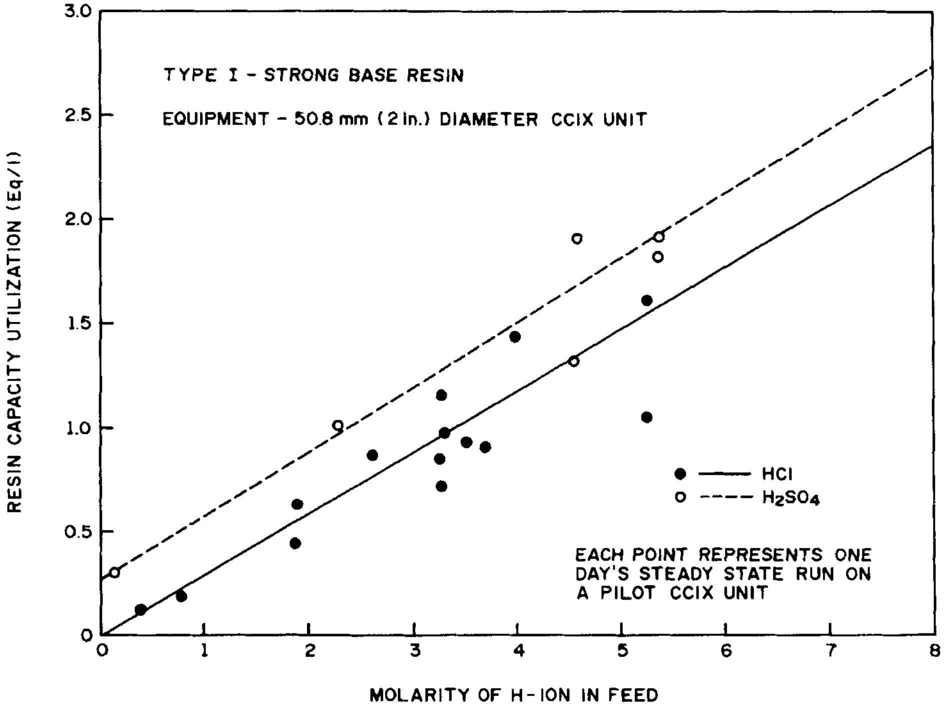

Figure 4. Acid Retardation - Capacity Utilization Versus Acid Feed Strength for HCl and H_2SO_4.

this. Hydrogen ions are crowded into the resin matrix not necessarily one per resin equivalent.

Although the mechanism of Acid Retardation is not proved for sure, it is thought to be a restructuring or denser packing of the H-ion within the resin particle. Basically, the exchanger distinguishes between H^+ and metal cations rather than acids and salts. The degree of H-ion uptake is related to total anion strength with total exclusion of metal cation, except for those that form metal anion complexes.

In reference to the resin-solution counterflow system depicted in Figure 3, feed acid is sorbed and travels with the the resins and metal contaminants pass on through uninhibited. By utilizing continuous countercurrent flow, economical use is made of the water strip to the point that the acid may be eluted no more diluted than the feed. The degree of separation of acid and metals may be controlled by refluxing or scrubbing with product acid. These options exhibit as inverse proportionality. To increase the degree of metal exclusion, the acid production rate can be decreased.

A most interesting and potentially useful aspect of Acid Retardation is that H-ion may be crowded into the resin bead relative to the total anion strength; not just the free acid strength. This means that acids may be concentrated as well as be separated, when bulk salts are present in the feed. For example, a solution 0.4N in HCl, in a total $CaCl_2$, KCl, HCl solution 3.6N, was concentrated to 2.0N HCl. An interesting way to express this is to say acid was increased 5 fold in strength when adding water. See Figure 5.

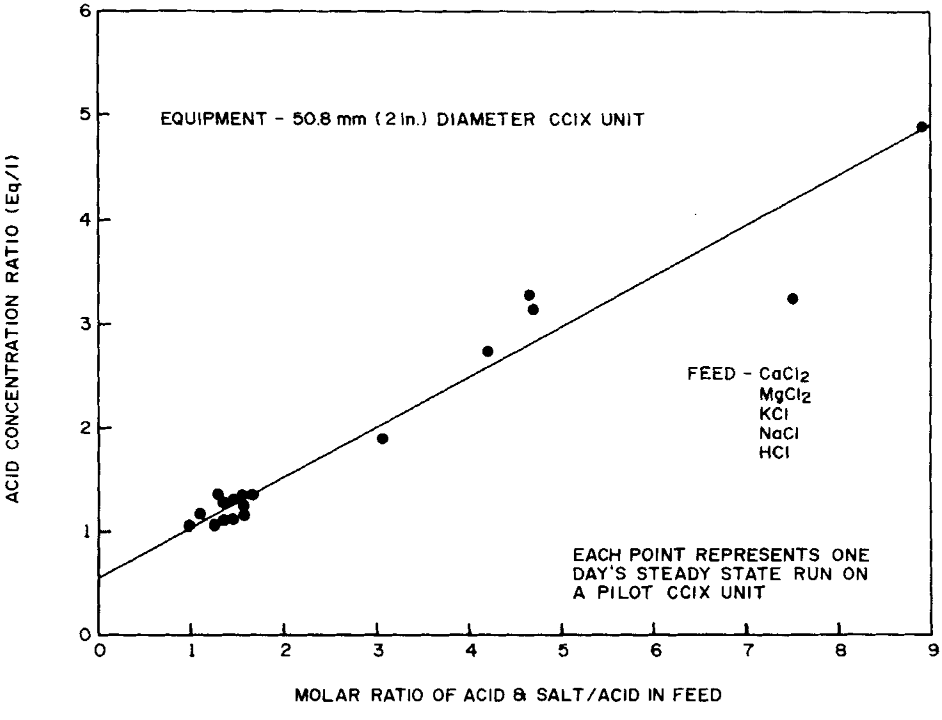

Figure 5. Acid Retardation Concentration of Acid Versus Salt Concentration in Feed Via CCIX Refluxing (Chloride System).

There is a striking difference in the water elution of a polyvalent acid like H_2SO_4 as compared to HCl or HNO_3. This is attributed to another and very different "acid sorption - water elution" system called Sul-bisul (Dow trade name) or "Site Sharing" (term coined by Fred Helfferich). For example, H_2SO_4 may be sorbed from dilute solution on sulfate form resin, R_2SO_4 to the bisulfate form $R\text{-}HSO_4$. The reaction is reversed by adding water.

$$R_2SO_4 + H_2SO_4 \rightleftharpoons 2RHSO_4 + H_2O$$

This is a system useful in certain water demineralization processes, but the reconversion to R_2SO_4 is inefficient just using water. Acid capacity utilization increases with acid strength, but it is difficult to distinguish where Sul-bisul stops and Acid Retardation takes over.

This great difference in the acid elution efficiency for HCl and H_2SO_4 using CCIX is depicted in Figure 6. This is interperted as a Sul-bisul effect acting independently from Acid Retardation. All poly-acids as H_2SO_4, H_3PO_4, etc, act by Sul-bisul and Acid Retardation. Monovalent highly ionized acids, such as HCl and HNO_3, use Acid Retardation only. Poorly ionized HF reacts by the Sul-bisul mechanism, and probably ionizes as follows:

$$H^+ + HF_2^- \rightleftharpoons H_2F_2$$

There is a special physical problem in loading acid from strong solution (low in salts) without avoiding dilution. The stronger the acid the higher the acid loading, but the lower the solution-to-resin flow ratio. Resin void volume in a packed column of uniform beads is 0.4. Whenever the F/R (Feed-to-Resin) flow ratio is less than 0.4, this means that there is not enough feed solution to occupy this void and displace its contained void volume of water. This causes dilution. By the definition of Acid Retardation, dilution causes less resin capacity utilization and increased acid loss. This effect is counteracted by recycling some of the highly conductive salt waste to displace this void volume water, or to avoid water intrusions. See Figure 3. Whenever there is trace acid with bulk salt, the F/R may be greater than 0.4 and this special recycle feature is not required.

Thus far, CSA has pilot demonstrated five systems; three with H_2SO_4 and two with HCl. The first was treatment of spent Al anodizing bath. The purpose was to recycle H_2SO_4 and reduce alkali consumption for neutralizing $Al_2(SO_4)_3$. About 90% of the acid was removed from the salt waste and about 90% of the Al from the acid product. One hundred percent separation could not be attained because of the Sul-bisul mechanism with H_2SO_4. Because of the inherent continuous countercurrent efficiency of the CCIX equipment used, neither the H_2SO_4 nor the $Al_2(SO_4)_3$ streams were diluted as compared to the feed.

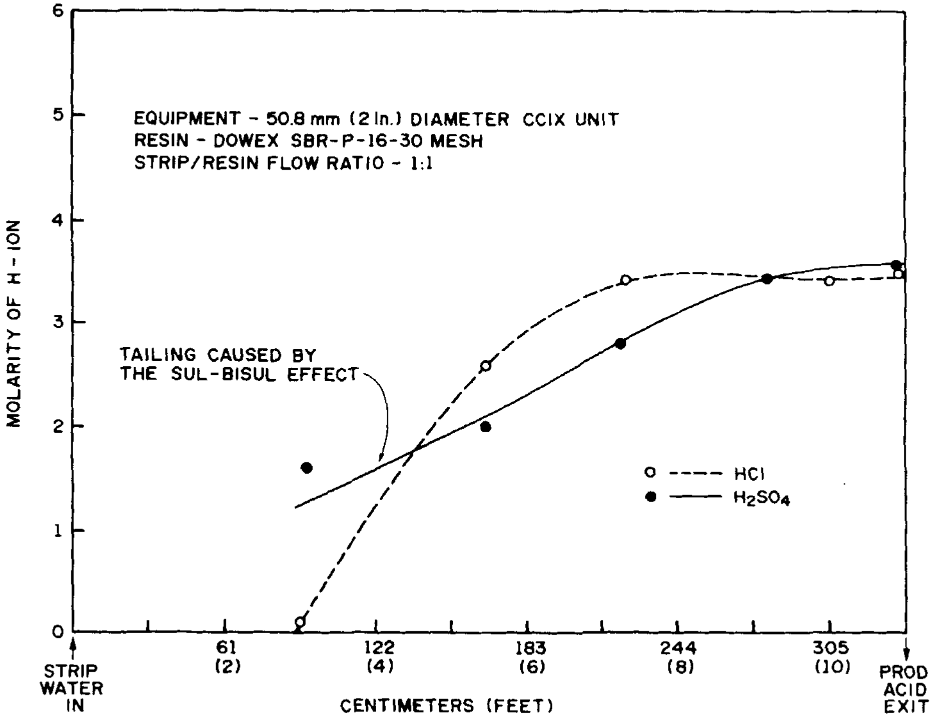

Figure 6. Comparison of Stripping Efficiency HCl Versus H_2SO_4.

Another sulfate system was with regenerant waste from a cation exchange treatment of Bright-Dip $AlPO_4 \cdot H_3PO_4$. Four normal H_2SO_4 is used as regenerant. The Al (plus Fe, Cr, Ni, Cu, etc.) is transferred from the H_3PO_4 to the H_2SO_4. This sulfate waste, undiluted from 4N, is sent through Acid Retardation. The H_2SO_4 is recovered with no dilution, with greater than 90% rejection or metals, and in suitable form for reuse as cation regenerant.

A third sulfate system was for recovery and recycle of lead storage battery acid. Specification for trace metals was very low; Fe, Sb, Ni, Mn, As, Zn, Cd, Cu, etc. Emphasis was placed on refluxing H_2SO_4 to scrub out metal contaminants. Production rate of product H_2SO_4 suffers somewhat to attain high degree rejection of metals because some is used for scrubbing, but one has the option to adjust this as needed.

One HCl system was a metal treating waste primarily made up of HCl·$AlCl_3$. The objectives were to prepare an acid-free $AlCl_3$ and to recycle HCl. The $AlCl_3$ was practically neutral at about pH 3.

Another chloride waste was about 3N and from a cation exchange regeneration. The bulk salts were Ca, Mg, K, and Na with traces of Fe, As, Al, Mn, Cr, Pb, and Ni. Again, the HCl was recovered slightly concentrated with a 90% to 95% elimination of metals.

An area that seems especially attractive for Acid Retardation is treatment of spent electrowinning cell liquors, both chloride and sulfate. Build up of acid in an electrowinning bath reduces current efficiency. This accumulated acid may be continually extracted, and concentrated, by Acid Retardation.

Another interesting utilization of Acid Retardation is to make strong acids from weak acid. No other ion exchange system is known for doing this.

The following weak-base resin reactions is common:

$$NaCl + H_2CO_3 + R^{\bullet} \longrightarrow R\text{-}HCl + NaHCO_3$$

However, the HCl on the resin cannot be removed as acid and must be neutralized.

The question here was, would the same reaction occur with strong-base resin by Acid Retardation? The acid could then be removed with water. In order to function, the Acid Retardation resin affinity for ionized H-ion had to be stronger than the coordinated bond of H-ion for the weak acid.

Nearly saturated NaCl, 4M, was mixed with a highly soluble weak organic acid, formic as 3M, which has an ionization of $K = 1.77 \times 10^{-4}$. The mixture was fed to a column of SBR and eluted with water.

As noted from Figure 7, chloride was taken up by the resin in the only form it could by Acid Retardation, as highly ionized HCl, with displacement of Na and formate.

A long range goal is production of ion exchange water treatment strong acids from lower cost sources or wastes of HCOOH, HAc, SO_2, and hopefully CO_2.

CONCLUSIONS

Two process extremes using Continuous Countercurrent Ion Exchange (CCIX) were chosen as examples. The first was a plant where the feed-to-resin flow ratio ranged from 500/1 to 1000/1, which is the paramount consideration when extracting a trace component from a very large volume. This application demonstrated

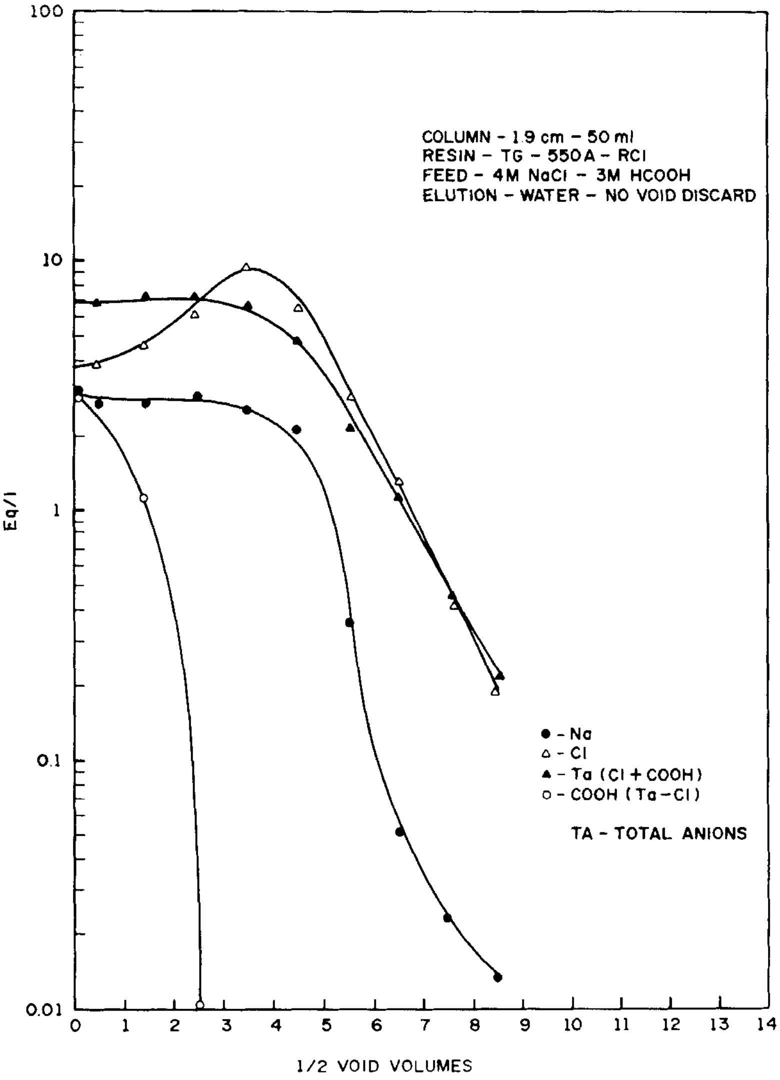

Figure 7. Production of Strong Acid from Weak Acid by Acid Retardation.

the recovery of 5 ppm of U_3O_8 from a sulfate leach of low grade copper ore. The second example was the adaption of Acid Retardation to CCIX where it is necessary to utilize very low solution-to-resin flow ratios in the range of 0.2/1 to 0.5/1. This must be done without dilution because, by definition, Acid Retardation only functions in strong solutions. These extremes of high degree performance; (1) high liquid throughput rate, and (2) maintenance of strong solutions, are inherent features of continuous countercurrent flow. The particular device described herein, known as the CSA CCIX system, mechanically allows such extremes of flow ratios to be achieved.

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