

## ACID SEPARATION FOR IMPURITY CONTROL AND ACID RECYCLE USING SHORT BED ION EXCHANGE

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### Abstract

Acid separation using short bed ion exchange is a now well established technology in copper refinery tankhouses. Refinery bleed streams from liberator cells are treated by short bed systems to produce an acid-free byproduct stream that contains the bleed metals and valuable nickel salts. Removing the acid eliminates the need for a black acid evaporator and reduces the amount of sodium carbonate required in nickel selective precipitation processes. The recovered sulfuric acid can be recycled to the tankhouse. This same technology is routinely used to treat other acids such as hydrochloric, nitric, and hydrofluoric. In the case of hydrochloric acid, the process can selectively separate chloro-anionic complexes such as Zn, Pb, and Cu, which are then eluted with water. The acid recovery technology can also be closely coupled with ion exchange processes in order to minimize regenerant acid consumption. In many hydrometallurgical applications resin regeneration often requires an acid dosage multiple times the stoichiometric minimum. Coupling an acid recovery bed with the IX column allows recovery and recycle of the free acid in the spent regenerant, thus reducing the overall acid consumption to just slightly more than stoichiometric.

### Short Bed Ion Exchange

The short bed ion exchange process has been extensively used in the metal finishing industries since the early 1970s [1,2]. Short bed systems have also been sold to primary metals producers for the separation of sulfuric acid from copper refinery bleed streams [3] and for the recovery of nickel and cobalt from plant effluent streams. This unique technology optimizes the ion exchange process and offers a number of significant advantages over conventional ion exchange. The principal features and benefits of this technology are presented below.

#### Fine Mesh Resins

Short bed technology uses resin beads with much smaller diameters than conventional ion exchange systems (approximately 20%). Reducing the size greatly improves the exchange kinetics. This allows operation at higher flow rates and reduces the length of the mass transfer zone. This is particularly important for chelating resins, which have very slow exchange kinetics. Work by Price [4] indicates that the exchange rate is inversely proportional to the square of the particle diameter. Thus, halving the particle size increases the exchange rate by 400%. The resulting higher flow rates significantly reduce the volume of resin required. This is

particularly important when using expensive chelating resins. Finer particles also aid in fluid displacement which allows a reduction in rinse volume requirements.

### Short Depth Resin Beds

During the operation of a fixed bed process, exchange takes place only in the fraction of the bed occupied by the mass transfer zone, MTZ. Upstream the resin has been exhausted, while downstream the resin remains in the regenerated form. Thus, in a conventional column the majority of the resin is inactive. The short bed process reduces the depths of these inactive regions and makes more effective use of the remaining resin. It should also be noted that the increased kinetics reduce the depth of the mass transfer zone to 0.15 - 0.61 m.

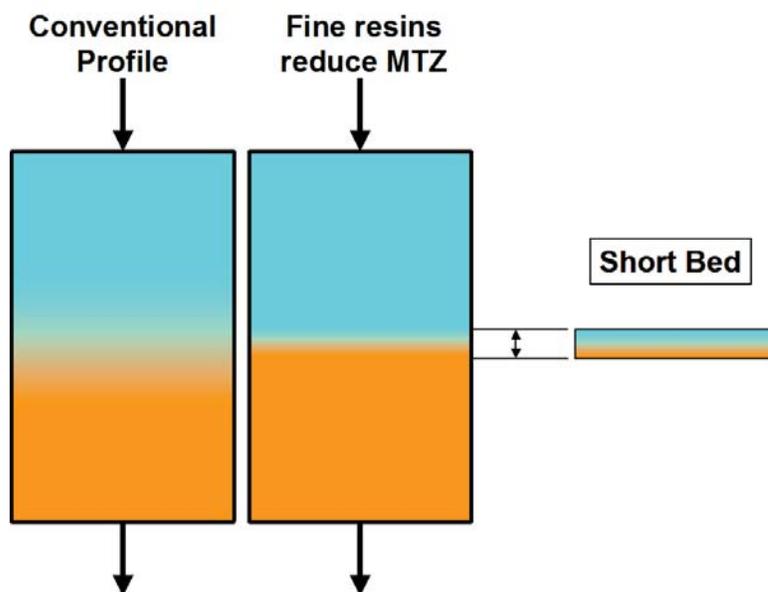


Figure 1. MTZ in short bed column

### Counter-Current Regeneration

Counter-current regeneration introduces the regenerant into the resin bed in the direction opposite to the feed solution. This technique is a well known chemical engineering principle which, in this case, helps to reduce the amount of regenerant required, maximizes the concentration of the recovered metal or acid and ensures complete regeneration minimizing leakage.

### Fully Packed Bed

In a short bed, the vessel is completely packed with resin leaving no freeboard. In a conventional column, mixing of the various solutions being processed occurs in the freeboard

space. The resulting dilution is very undesirable when processing concentrated solutions. A packed bed eliminates this dilution and also helps to maintain the concentration profiles developed within the resin bed. This ensures that the benefits of counter-current regeneration are fully realized.

Although these features offer many benefits the following disadvantages should be noted. Unfiltered feed solutions will quickly foul fine mesh resins and a packed bed does not allow fluidized backwashing of the resin to remove any entrained solids. Thus it is necessary to properly prefilter all solutions fed to a Recoflo bed. Also, fine mesh resins are not standard materials and as a result are more expensive on a per unit basis and can be more difficult to obtain.



Figure 2. Fully packed short bed system

### **Acid Separation**

Short bed technology has been adapted to acid separation and is provided as an acid purification unit, APU. This process uses ion exchange resins that selectively absorb free acid but reject dissolved metal salts. The absorbed acid can be removed by passing water over the resin. Although the use of a specific type of ion exchange resin is required, the process is strictly speaking not ion exchange. The acid is not exchanged onto a specific site and the process capacity is not limited by the ion exchange capacity of the resin. The process is driven by the acid concentration difference between the interior of the resin phase and the surrounding fluid.

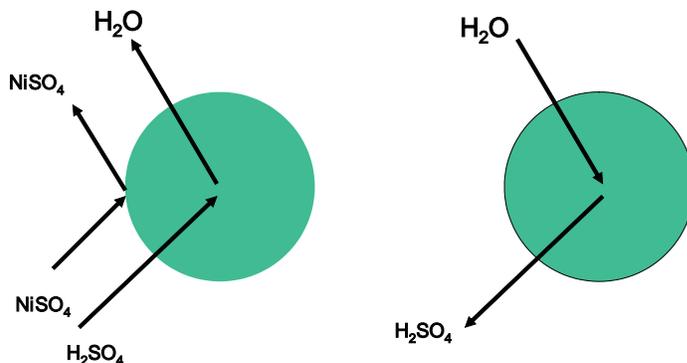


Figure 3. Acid sorption and de-sorption

Typically, only a small volume of solution, less than the volume of the ion exchange resin bed, can be processed during each cycle. This restriction coupled with the standard engineering design for most ion exchange processes delayed the successful commercialization of the acid retardation process until the late 1970s [1]. Since short bed technology uses a packed column and counter-current regeneration, the problems associated with dilution and control faced by conventional designs are overcome.

In 1979 the first APUs were installed in the aluminum industry to recover sulfuric acid used in anodizing operations [1]. Since then, the APU has been used for the recovery of many different acids in many different industries, including the treatment of hydrometallurgical streams [3,5]. To date, over 300 units have been installed worldwide. The majority of these units have been installed in the metal finishing industry.

#### APU Operating Cycle

The first step in the APU process is to filter the feed through a multi-media sand-type filter. This is then followed by cartridge polishing filters located on the unit.

The APU operating cycle, which normally lasts about 4 - 5 minutes, is divided into an upstroke and downstroke as shown in Figure 4. During the upstroke, feed solution is pumped up through the APU resin bed. Initially the interstitial void volume in the resin bed is filled with water from the previous cycle. The incoming filtered feed displaces this water, which is then collected as the water void; this is transferred to the water tank and used along with additional make-up water during the downstroke. As the feed continues to pass over the resin, the acid is absorbed into the bead and thus its passage through the resin bed is "retarded". The metal salts are rejected by the resin and they breakthrough into the effluent or byproduct stream ahead of the acid. The upstroke is completed just as the acid begins to breakthrough into the byproduct.

During the downstroke, water is pumped downward through the bed. Initially the bed void is filled with unseparated feed solution. This feed void is displaced by the incoming water back into the feed tank for processing during the next cycle. As the water continues to pass through the bed, the majority of the metal is displaced and the purified acid removed during the upstroke is de-sorbed and collected as the product. The purified acid product concentration may range anywhere from 50 - 110% of the feed value depending on the operating conditions and the feed concentration. By adjusting the volumes and flow rates of these various process steps it is possible to optimize APU performance depending on the process objectives. Typical process capabilities range from 70 - 95% acid recovery and 50 - 90% metal removal.

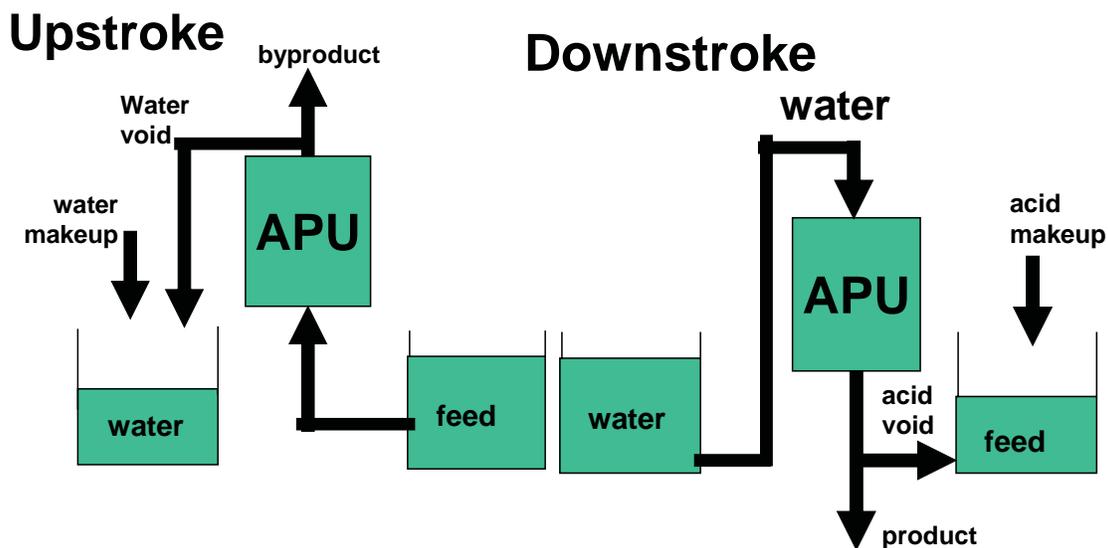


Figure 4. APU upstroke (acid loading) and downstroke (acid desorption)

**a e S t d   A c i d   S e p a r a t i o n   r e p o r t   c o n t a i n i n g   a o e a**

The El Paso copper refinery has been in operation since 1930 and by 2006 had reached a production capacity of 430,000 tons of cathode copper per year. As the city of El Paso has grown around the refinery, attention to unique environmental considerations specific to this location are of prime importance in all endeavors of operation. The entire facility is a zero discharge operation with only a small amount of potable water allowed to be sent out to the local POTW.

For many years, discard electrolyte solution from the tank house was treated via a nickel circuit for nickel recovery. The technology employed was vacuum evaporation for the crystallization of nickel sulfate. These crystals would be separated by a centrifuge and packaged for market. The resulting waste solution was a black acid liquid material that needed to be transported off site by rail car. Fresh, concentrated sulfuric acid was used to make up the acid losses encountered in the

tank house as a result of this method. In 2002, the age and condition of this equipment was such that it needed to be replaced or intensely refurbished.

### System Operation

The system selected and installed to replace the existing evaporator/crystallizer system involved the use of an Acid Purification Unit (APU) to deacidify the liberator electrolyte bleed solution in order to recycle the recovered sulfuric acid, followed by two stage precipitation to obtain a purified, salable nickel carbonate byproduct.

The process is such that an electrolyte bleed solution from the existing liberator cells is delivered to the system. A backwashable media filter is used to remove suspended solids from the solution. Filtered solution is then transferred to the APU feed tank. Feed solution is pumped through the APU where acid is sorbed by the ion exchange resin material while the metallic salt impurities pass through to the byproduct. This byproduct stream consists of the metallic salts and a small amount of free sulfuric acid. Water used for 'regeneration' of the ion exchange resin is pumped down through the APU resin bed from the APU water tank so that the sulfuric acid is desorbed as a product solution. This purified solution exits the APU and is collected for reuse within the tank house.

### System Performance

Typical process specifications around the APU subsystem are shown in Table I. Up to 3.2 m<sup>3</sup>/h of liberator bleed solution are processed resulting in a nickel removal rate of up to 36 kg/h. The APU shown in Figure 5 is 1.4 m in diameter and 0.6 m in depth with a resin volume of 0.9 m<sup>3</sup> and can treat a maximum flow rate of 4.2 m<sup>3</sup>/h.

Table I. APU System Performance

<b>Strea</b>	<b>S</b> (g/L)	<b>i</b> (g/L)	<b>(g/L)</b>	<b>o</b> m <sup>3</sup> /h
Feed	275	15.00	5.00	3.2
Acid Product	240	3.75	1.25	3.2
Metal Byproduct	35	11.25	3.75	3.2
Water	---	---	---	3.2
Loss / Removal	12.75%	75%	75%	---

Typical performance indicates an acid recovery rate of greater than 87% and a nickel removal rate of greater than 75% through the APU system. Other metallic contaminants such as copper and iron are removed at the same efficiency. The majority of the arsenic follows the sulfuric acid back to the tank house (typically only 10 – 15% removal). This perceived poor removal efficiency associated with arsenic is of much benefit in enhancing quality and productivity issues within the tank house. Removal efficiency for contaminants such as antimony and bismuth is on the order of 50%.

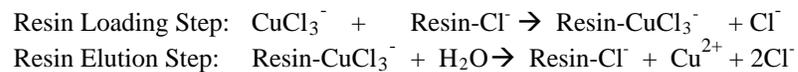


Figure 5. The APU System at the El Paso Refinery

### Acidic Solution Separation and Recovery

It is well known that various metals form chloro-anionic species in HCl. The formation and stability of these complexes depends on the concentration of chloride. Such complexes will exchange onto the APU resin. Washing the resin with water decomposes the loaded complex and liberates the metal.

In the production of carbon steel, mill scale is removed by counter-current pickling of the steel strip in 6N HCl. The recycle of scrap steel has resulted in the introduction of copper into the pickle acid. This copper will cement out onto the steel strip producing undesirable pink steel. Cu(II) forms an anionic Cl complex that can be removed by the APU resin according to the following reactions.



The volume of solution that can be processed by the APU when removing Cu in this manner is much larger than when treating a stream where the process objective is acid separation. Typical performance of an APU system on such a stream is shown in Table II below.

Table II. APU Performance for separation of Cu from HCl

Stream	Bed Volume (BV)	f-HCl (N)	t-Cl (g/L)	Cu (mg/L)	Fe (g/L)
Feed	7.0	0.81	161.8	310	129.3
Raffinate	7.0	0.39	158.1	0.5	111.2
Strip	1.0	3.05	102	2030	59

Zn also forms a strong anionic complex in HCl. Zn removal from HCl is a requirement when using SX to recover Co as the Zn fouls the solvent. Figure 6 shows the loading and elution profiles for Zn removal by an APU. Table III presents typical APU performance for this application.

Table III. Zn and Co separation from HCl

	Volume (BV)	Co (g/L)	Zn (g/L)	HCl (eq/L)
Feed	29.0	8.4	1.13	3.3
Product	29.0	7.6	0.03	3.2
Feed Void	1.0	15.5	2.68	2.3
Waste	8.9	0.2	3.28	pH=2.5

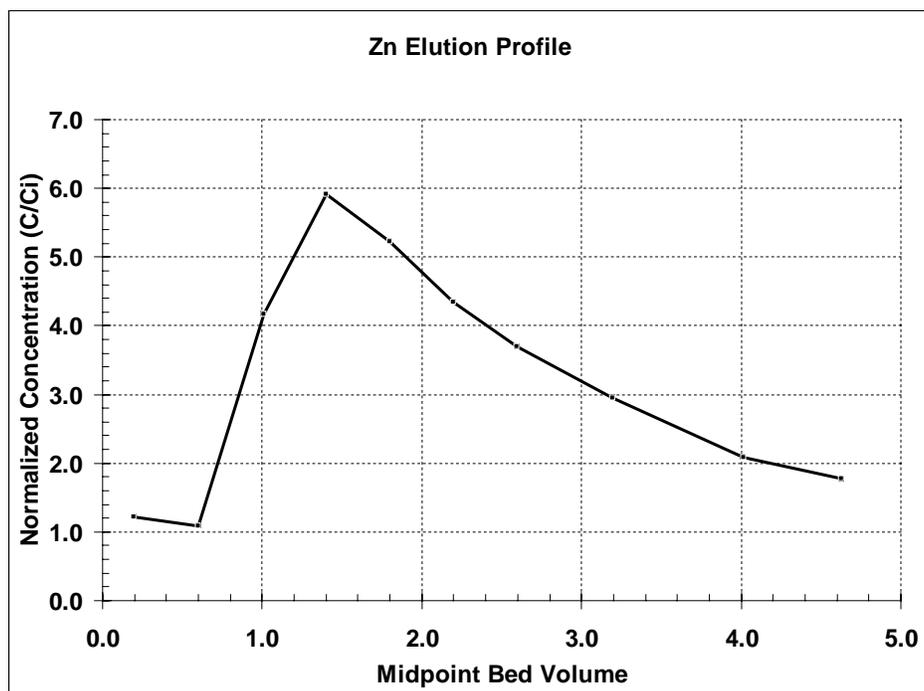
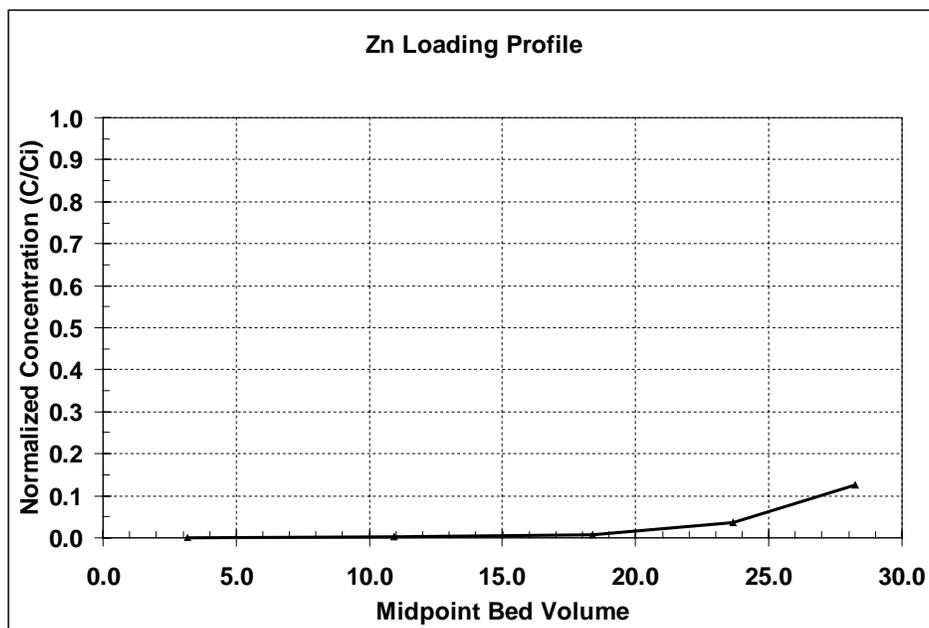


Figure 6. APU loading and elution profiles for Zn

**a e S t d e c o e r    A c i d r e g e n e r a n t r e c o v e r y p r o c e s s**

Many ion exchange processes use large quantities of regenerant acids, often well in excess of the stoichiometric requirement. This is particularly true when the selectivity of the resin is high for the ion of interest, as is often the case with multi-valent cations like Al or Fe. In such cases it is possible to use the APU process to treat the spent regenerant acid. This separates the dissolved metal salt and allows the purified acid to be re-used as a regenerant.

When used to recover regenerants in this manner, a coupled bed system known as a DPU is used (Figure 7). The ion exchange resin bed is used to remove the ion of interest from the process solution. Then during regeneration, the acid flows in series first through the ion exchange resin bed and then through the APU bed where the excess acid is removed before the waste is discharged. The acid is recovered from the APU bed by counter-current washing with water. The recovered acid liberated from the APU resin flows back through the ion exchange bed and into the regenerant acid tank for re-use during the next cycle. A small amount of concentrated make-up acid must be added to account for the acid exchanged onto the resin and the small amount lost in the waste.

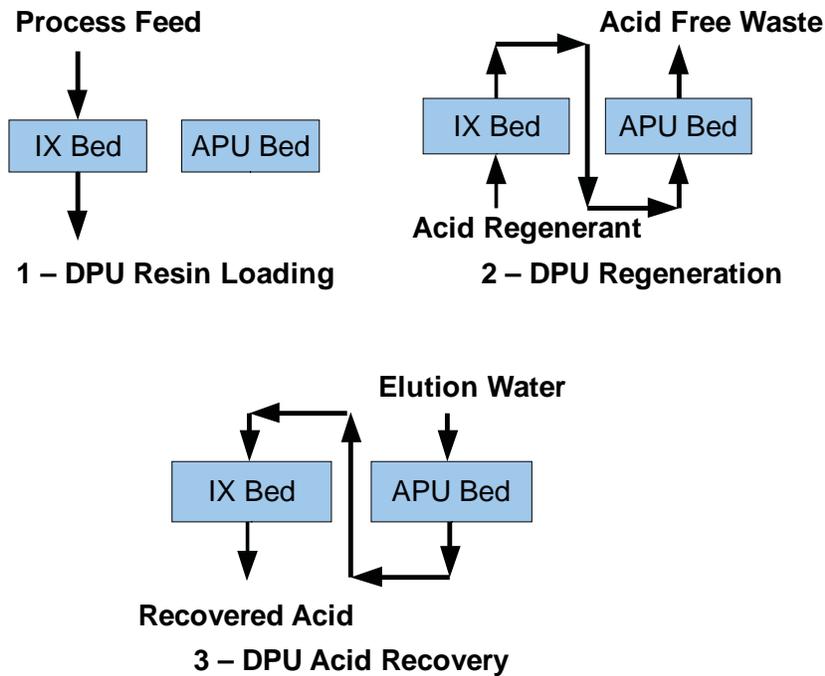


Figure 7. DPU – IX acid regenerant recovery process

Phosphoric acid is used in the brightening of aluminum. As the parts are processed, the acid bath becomes contaminated with Al, And this affects the brightening process. Typically the Al is removed from the solution both via solution drag-out on the parts and by a direct bleed. The

Phosphoric acid in this contaminated solution is valuable and can be recycled if the Al can be removed.

Ion exchange using a strong acid cation resin can be used to remove Al from this solution. The very high concentration of phosphoric acid (85% w/w) requires dilution to permit the exchange and to reduce the viscosity. The strong preference of this resin for Al requires that a large excess of fairly concentrated sulfuric acid be used to regenerate the resin. A typical concentration would be 20 – 40% w/w H<sub>2</sub>SO<sub>4</sub> with a dosage that might be 5-10 times the stoichiometric requirement.

Typical overall performance for such a DPU system is shown in Table IV and the process equipment is illustrated in Figure 8. In this case, the cation resin bed is regenerated with 1.4 bed volumes of 37% w/w sulfuric acid. This is equivalent to a regenerant dosage that is 9.7 times the stoichiometric minimum required to exchange the Al. The spent regenerant stream is pumped in series through the APU bed removing the unconsumed sulfuric. The net result is a waste stream of only 0.6 BV, containing less than 3.5% sulfuric acid, with an overall net regenerant dosage of only 1.5 times the stoichiometric amount.

Table IV. DPU process performance

<u>Input Streams</u>	<b>Volume (Bed Volumes)</b>	<b>Al (g/L)</b>	<b>PO4 (g/L)</b>	<b>H2SO4 (g/L)</b>
<b>Concentrated Incoming Feed</b>	1.6	8.8	350	
<b>Concentrated Sulfuric Acid to Make Regenerant</b>	0.06			1,728
<b>Dilution and Wash Water</b>	4.64			
<u>Output Streams</u>	<b>Volume (Bed Volumes)</b>	<b>Al (g/L)</b>	<b>PO4 (g/L)</b>	<b>H2SO4 (g/L)</b>
<b>Purified H3PO4 Product</b>	2.1	0.9	240	
<b>Concentrated Waste Regenerant</b>	0.6	18.6	40	
<b>Feed Rinse to Waste</b>	1.4	0.05	20	
<b>Recycled Regen Water</b>	0.8	0.77	1.5	
<b>Dilute Regen Waste</b>	1.4			



Figure 8. Full scale DPU system used in Japan

## S ar

The use of short bed ion exchange for acid separation is now very well proven technology. More than 300 acid purification systems, APUs, have been supplied since 1977. The technology has found application in hydrometallurgy for the treatment of refinery bleed streams. A case study for one such installation has been presented in this paper. Additional case studies have been presented that show how the technology is used for the separation of chloro-anionic complexes from HCl and how it can be applied for the recovery of excess acid from spent ion exchange regenerant streams.

## erence

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