

# MIXED ACID RECOVERY with the APU™ ACID SORPTION SYSTEM

CRAIG BROWN, Prosep Technologies , Eco-Tec Inc., Pickering, Ontario

## An Update

---

### SUMMARY

Since the first APU™ acid sorption system was installed in 1982 for recovery of mixed nitric/hydrofluoric acid stainless steel pickle liquors, the industry has embraced the technology, so that by now most mills have installed systems of this type. Although the basic technology has been available for more than twenty years, the APU system has been enhanced through improved flow distribution, filtration, analytical tools and process controls.. Safety concerns about treatment of nitric acid have been addressed by cooling the pickle prior to treatment. This paper will review these developments and discuss some new innovations that are coming in the future.

Keywords: **nitric acid, hydrofluoric acid, ion exchange, stainless steel, pickle, recovery**

### 1. INTRODUCTION

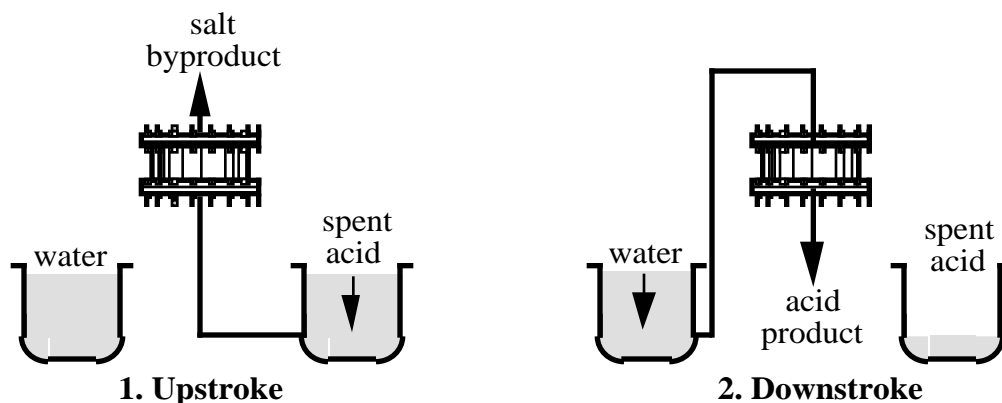
In 1963 a new process for separation of strong acids from metal salts was introduced by Hatch [i]. Called 'acid retardation', the process held considerable promise for purification of waste acids generated in pickling metals and leaching ores. The primary appeal of the acid retardation process is that the acid that is sorbed by the ion exchange resin can be recovered by a simple water elution. Consequently, economical recovery of a chemical as cheap as sulfuric acid can be contemplated. Although a few early attempts were made to commercially exploit the process, it was not until 1977 when Eco-Tec introduced a system called the APU® (acid purification unit) for purification of sulfuric acid anodizing solutions [ii] that the process became commercially viable. This process very quickly became accepted by the aluminum finishing industry around the world, with hundreds of units being installed.

Over the ensuing years a large number of APU's were installed on a wide variety of applications, including steel pickling baths. Although these included sulfuric and hydrochloric acid carbon steel pickling baths, it quickly became evident that the economics of recovering hydrochloric and sulfuric acid pickle liquors were marginal. A much more attractive application was purification of stainless steel pickle liquors based upon mixed nitric/ hydrofluoric acid. In 1982 the first APU was installed on a stainless steel pickling application. Since that time over seventy units have been installed in fifteen different countries. In addition to the cost savings, a number of productivity improvements have been identified when an APU system is operated [iii].

### 2. BASIC APU PROCESS DESCRIPTION

One of the reasons that it took so long for the acid retardation process to become commercialized is that conventional ion exchange designs, originally developed for treatment of large volumes of water, are not well suited to the treatment and production of small volumes of concentrated liquors. A key to the success of the acid retardation process has been utilization of a novel ion exchange process called Recoflo™, which was originally developed at the University of Toronto. The original Recoflo process is characterized by the use of short beds of fine mesh ion exchange resins, operated in a counter-current flow scheme.

There are two steps in the basic Recoflo APU process - the "upstroke" and the "downstroke" (see Figure 1). During the upstroke, spent acid is pumped into the bottom of the resin bed. Acid is sorbed by the resin particles and the remaining de-acidified metallic salt solution, designated arbitrarily as the "byproduct" is collected from the top of the bed. Next, during the downstroke, water is pumped into the top of the bed, desorbing the purified acid from the resin so that a purified acid "product" is collected from the bottom of the bed. Control is achieved by measurement of stroke volumes. The total cycle typically takes about 5 minutes to complete and repeats successively.



**Figure 1: APU Operating Cycle**

### 3. IMPROVED FLOW DISTRIBUTION

Since in the acid retardation process only a relatively small volume of acid can be treated during each sorption cycle, the challenge lies first of all, in minimizing the amount of water employed for the elution step, to avoid diluting the recovered acid. Secondly, to maximize the purity of the recovered acid, it is important to minimize mixing of the contaminated feed acid with the purified recovered acid. The original Recoflo process went a long way to addressing these issues by using a fully packed bed resin bed and essentially eliminating the freeboard above the resin that is found in conventional ion exchange columns.

In the mid 1980's it was found that the efficiency of the Recoflo process could be further enhanced by improving the uniformity of flow distribution of fluid passing through the bed. This was accomplished by packing the resin bed in such a way such that the resin is always maintained in a state of compression, even when the resin has shrunk. This patented [iv] technique is called 'over-packing'.

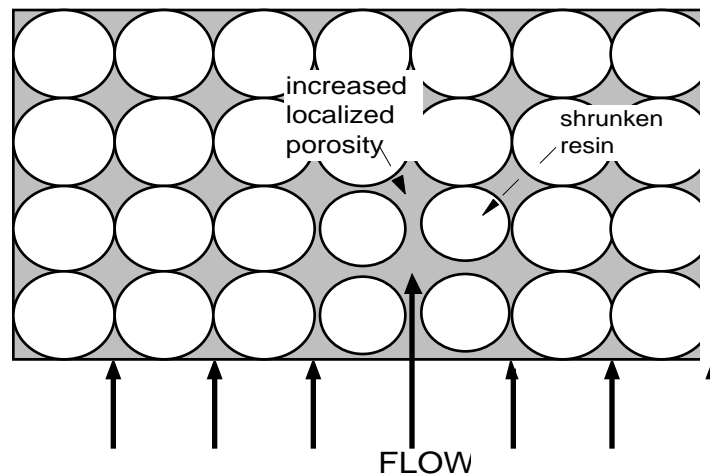
It is well known that ion exchange resins change volume as they are converted from one ionic form to another and when the concentration of the surrounding solution is changed. For example, resins normally shrink in concentrated solutions such as acids and they swell again when placed in water. This volume change, which is reversible, can be as much as 10% and has a significant effect on flow distribution.

Figure 2 represents a bed of resin in which the resin just fills the vessel at the start of the upstroke or acid sorption step, ie. just after the downstroke or water elution step has been completed. In this case, the resin bed fully occupies the space in the vessel and could be considered 'packed' but not yet 'over-packed'. In other words the resin is not under compression by any force other than that of gravity. The bed at this point is relatively uniformly packed however, with each resin bead in contact with the adjacent beads.

No flow distribution system is perfect, so that when the acid enters the bottom of the bed, acid will initially touch some portion of the resin bed slightly before another location. As discussed above, the resin at this point of initial contact will shrink when it is contacted by the acid. This will increase the space between the resin beads at this point (ie. increase the local bed porosity) and therefore reduce the liquid pressure drop at this point. The reduced pressure drop will accelerate the flow of the acid through the bed at this point, thereby causing a flow channel to develop. As more acid is pumped into the resin bed, the flow channel becomes more pronounced and propagates through the bed. The net result of this is that the flow distribution is adversely affected to a significant extent. In practical terms, this results in a slightly higher concentration of free acid in the de-acidified metal salt byproduct or waste produced by the unit and a slightly higher concentration of metal in the purified acid product.

Under over-packed conditions, when the acid initially contacts the resin and causes a portion of the resin to shrink as discussed above, some of the compressed resin from the surrounding region flows into the space developed, relieving a portion of the resin compression (see Figure 3). As a result, there is no localized increase in the bed porosity and no flow channels develop.

Typical performance results for a recent APU installation are shown in Table 1. It can be seen that 98% of the free hydrofluoric acid and virtually all of the free nitric acid values have been recovered. Seventy percent of the metals have been removed from the purified acid product. It should be noted that it is possible to further improve the metal removal efficiency by adjustment of the unit operating conditions, although there is really no benefit in doing so.



**Figure 2: Flow Channeling in a Packed Bed**

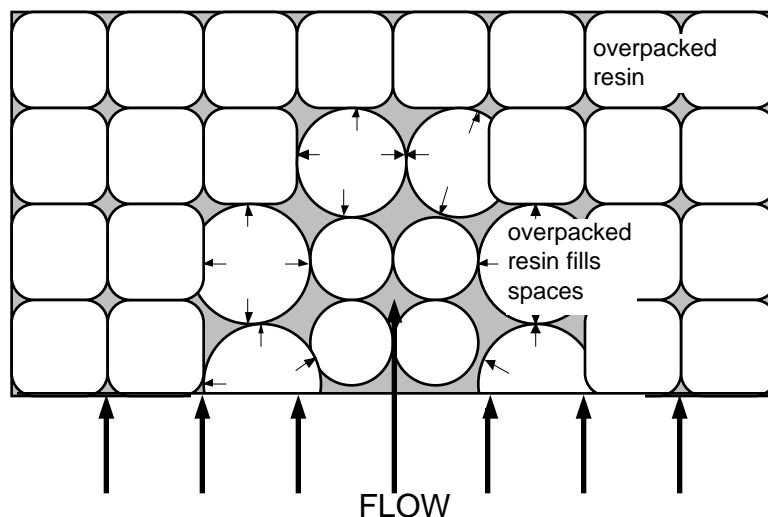


Figure 3: Improved Flow Distribution in an Over-Packed Bed.

**Table 1: Recent APU Field Results With An Over-Packed Bed**

	Volume (L/Lfeed)	Free HNO3 (g/L)	Free HF (g/L)	Total metals (g/L)
Feed	1	107	19.3	45
Product	1.01	104	18.5	12.6
Byproduct	1.0	0	0.3	30.4
Mass balance		-1.9%	-1.7%	-3.9%

#### 4. CHEMICAL ANALYSIS

In order to properly evaluate the performance of an APU system it is necessary to have a way to accurately analyze the chemical composition of all the streams entering and leaving the unit. A significant advancement in the analysis of stainless steel pickle liquors was the development by Lindroos [v] of a ion selective electrode (ISE) technique for free hydrofluoric acid. Unlike conventional ISE methods, the Lindroos technique does not require dilution of the sample. Moreover, unlike the conventional procedure, the Lindroos technique provides a measure of *free* hydrofluoric acid rather than *total* fluoride. This technique does suffer from a number of disadvantages however, including:

1. The HF electrode has a limited lifetime.
2. The output from the electrode is very sensitive to temperature variations resulting in a significant potential source of error.
3. The HF electrode requires frequent re-calibration.

Two commercial systems that utilize this novel ISE technique have been introduced for analysis of mixed acid stainless steel pickle liquors. The Scancon SA system takes a density measurement and an

expanded scale pH measurement along with the ISE measurement. Concentrations of nitric acid and total metals are then empirically calculated. While this technique is quite simple and quick, it suffers from a couple of disadvantages: First of all, the life of the proprietary pH electrode, which is rather expensive, is limited. Secondly, the accuracy is not particularly good, especially for APU byproducts, where the concentration of free acid is very low and the metals concentration is very high.

Eco-Tec offers another analytical technique which utilizes the ISE HF measurement. In the Eco-Tec ADI1000 and ADI 2000 systems, the ISE measurement is complemented by a proprietary automated titration. The titration procedure provides total free acid and total metal concentrations. The free nitric acid is calculated by subtracting the free HF number (from the ISE) from the total free acid number. The major advantage of the ADI system is its high accuracy. The excellent mass balance shown in Table 1 is an indication of the accuracy of the ADI system. Although it takes 10-20 minutes to complete one analysis with the ADI, which is somewhat longer than with the Scanacon unit, the procedure is totally automated.

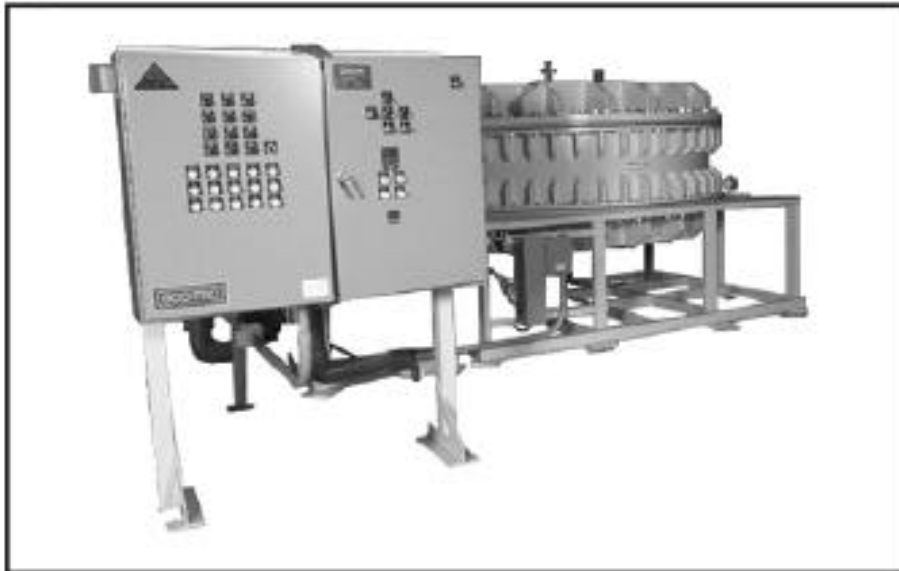
Recently, Eco-Tec has developed an improved technique for analysis of mixed acid pickle baths. The Eco-Tec ADI 5000 eliminates the use of pH and ISE probes as well as the titration. The unit takes a couple of quick physical/chemical measurements and then calculates free nitric acid, free hydrofluoric acid and total metal concentration, providing results virtually in real-time. This analyzer requires almost no maintenance or recalibration and none of its components require regular replacement. Because of the simplicity and rapidity of the technique, it is ideally suited to automated online sampling and measurement of pickle bath compositions. It can also be easily integrated into a full chemical management system to provide automatic maintenance of pickle bath composition.

## 5. APU SCALE-UP AND SCALE-DOWN

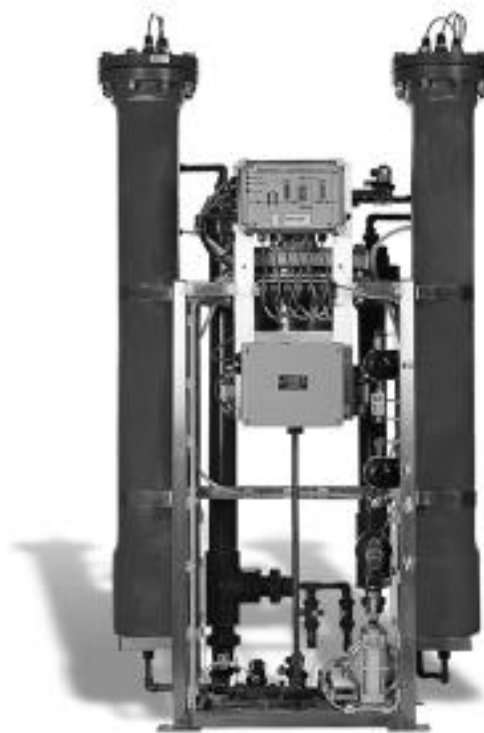
The original development work on the APU was done on a pilot plant with a 5 cm (2 inch) diameter bed. In 1986, the largest diameter commercial scale APU was 122 cm (48 inches). Since that time, new equipment designs have allowed for further scaleup. The largest unit to date is equipped with a 274 cm (108 inch) bed (see Figure 4), which is a scale-up factor over *five times* over the 122 cm unit. Results for this large unit as good as for the smaller units. For large installations, the use of large equipment like this eliminates the need for multiple units and therefore provides a number of advantages, including:

1. reduced complexity.
2. reduced space requirements .
3. reduced capital cost.
4. reduced monitoring and maintenance requirements.

There are a large number of small, batch operations used for pickling sheet and tubes. The potential savings for these operations is much less than a large continuous strip line due to the fact that less chemicals are consumed in the pickling operation. A new APU design called *Micropur*, which uses resin beds up to 50 cm (20 inches) in diameter has recently been introduced to provide an economical solution for this market. Micropur utilizes a standard, compact, economical 'off-the-shelf' design. Features of the Micropur unit include a stainless steel frame, graphics panel and integral acid and water reservoirs. Similar designs have previously been successfully used in the aluminum anodizing and electroplating markets. A typical Micropur unit is shown in Figure 5.



**Figure 4: Large APU with 274 cm (108 inch) diameter resin bed**



**Figure 5: Micropur APU for small pickling operations.**

## 6. FILTRATION

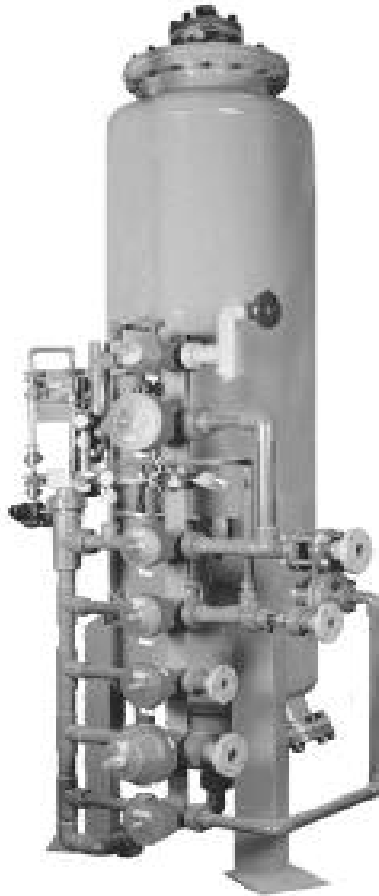
A major consideration in the design of an APU system is adequate filtration of the pickle liquor prior to treatment. The fine resin beds employed in the APU will plug-up with any suspended material that is not filtered out prior to treatment. While it is possible to clean the resin, the procedure is somewhat messy and a better solution is to provide proper filtration in the first place. A side benefit to removal of suspended solids is a reduction in plugging of the spray nozzles in the pickle tub.

Pickle liquor can contain a wide distribution and concentration of suspended solids. Analysis of several different tubs has shown that particle sizes range from  $<0.5 \mu\text{m}$  up to  $30 \mu\text{m}$ . Suspended solids concentrations have been measured from 9 mg/L to 800 mg/L. Sulfuric acid pre-pickles can contain appreciable quantities of undissolved scale and therefore have much higher suspended solids levels (300- 10,000 mg/L).

While disposable polypropylene cartridges can be used if their micron rating is fine enough, the suspended solids concentration normally present in most pickle liquors would make cartridge life prohibitively short. Sedimentation systems have not proved to be very effective. Solids do not settle out efficiently due to the high specific gravity of the liquor as well as convection currents present in the solution due to cooling through the tank walls. A further disadvantage of sedimentation systems is that the slurry withdrawn from the bottom of the clarifier contains an appreciable quantity of pickle liquor. Treatment and disposal of the 'bottoms' is expensive and the contained acid can represent a significant amount of lost value.

Excellent success has been obtained using a special dual-media filter design (see Figure 6). This filter has been shown to be effective in removing particles as small as 1 micron in diameter. The dual-media filter utilizes two permanent layers of filter media. Both of these media are totally resistant to chemical attack by the aggressive mixed acid solution being processed. The top layer, which is a coarse particulate material, removes the majority of the suspended solids. The bottom layer is much finer and removes the last traces of suspended solids. Because the filter media never need to be replaced, operating costs associated with the dual-media filter are very low. A cartridge filter is normally placed after the dual-media filter for redundancy, but experience has shown that due to the highly efficient action of the dual-media filter very little material collects on the cartridges.

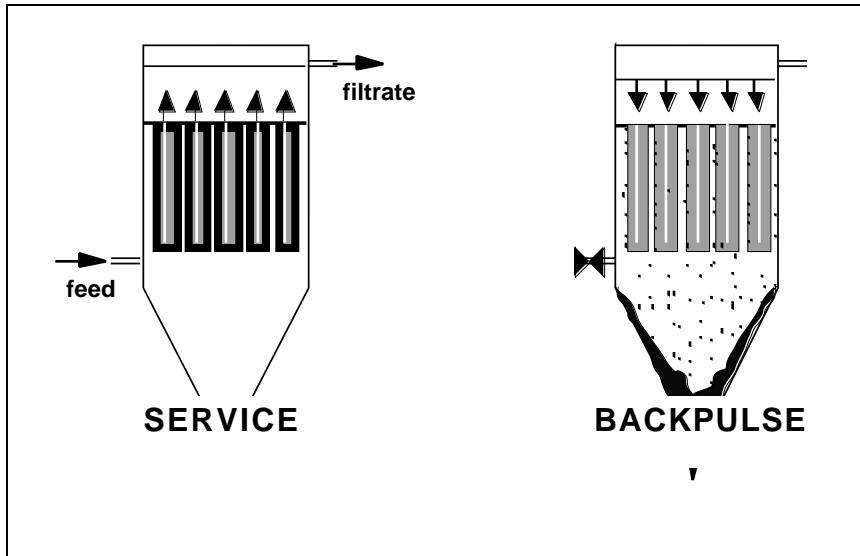
Plugging of the dual-media filter is accompanied by increased pressure drop, at which point it must be cleaned. In the first step of the cleaning procedure, the entrained pickle liquor is purged from the filter vessel with compressed air. By doing this, minimal quantities of free acid are lost from the system from the filter. The filter is then back-washed with water. This fluidizes the media and displaces the particulate contaminants to waste. In some cases, the filter is back-washed with byproduct solution from the APU instead of fresh water, in order to minimize wastewater. After the filter has been back-washed, the entrained water (or byproduct solution) in the vessel is drained using compressed air, to avoid dilution of the pickle liquor. The filter is then returned to service.



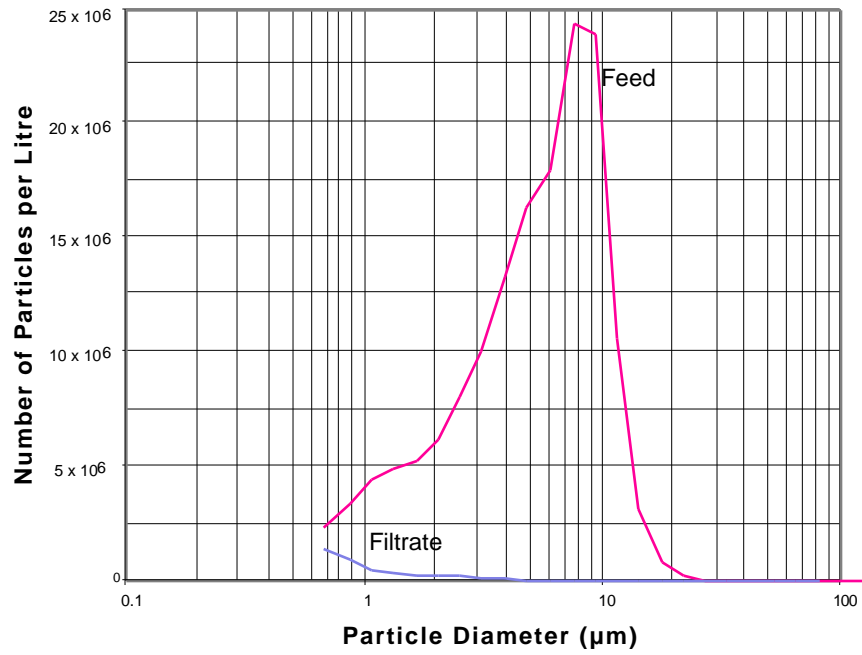
**Figure 6: Dual-Media Filter**

In some cases the concentration of suspended solids is too high to be effectively treated with a dual-media filter. This can occur in the sulfuric acid pre-pickle before the mixed acid pickle or where hot-rolled ferritic stainless steels are pickled in nitric rich baths. A different filter design has been developed for such applications. This filter, which is called a *pulse filter*, is based upon a design that has been extensively used in the pulp and paper industry for filtration of solids concentrations as high as 10% from kraft white liquor.

The design and operation of the pulse filter is shown in Figure 7. The pulse filter utilizes polypropylene 'socks' as a filter media. The socks are suspended vertically from a tube sheet inside a pressure vessel.. Feed is pumped into the filter vessel and clear filtered liquid passes through the socks and is collected in a chamber located immediately above the tube sheet. Filtrate overflows from this chamber to the APU feed tank. Solids accumulate on the surface of the socks as a thin filter cake and the pressure gradually increases as the service cycle proceeds. When the differential pressure across the socks reaches a predetermined level, the feed flow is stopped and filtrate is allowed to drain by gravity from the upper chamber back through the socks, thereby dislodging the cake from the surface of the socks. The relatively large cake solids settle to the bottom of the filter vessel, where they thicken to a solids concentration of about 10-20% w/w. Periodically, sludge containing the solid contaminants is withdrawn from the bottom of the filter and either purged directly to waste or de-watered in a small filter press so that the contained pickle liquor can be recovered. A back-pulse typically occurs every 5-30 minutes and lasts less than one minute. The extremely good particle removal efficiency for a pulse filter is illustrated in Figure 8.



**Figure 7:**  
Pulse Filter  
Operating Cycle



**Figure 8: Particle Removal Efficiency of Pulse Filter**

## 7. RESIN STABILITY

All manufacturers of ion exchange resins discourage the treatment of nitric acid with ion exchange resins such as those employed in acid retardation systems [vi,vii,viii,ix,x,xi]. This is because nitric acid can, under certain conditions, react violently with the resin. Extensive experience over the past eighteen years has shown that treating nitric acid with an acid retardation system is safe, providing proper precautions are taken in the design and operation of the system.

In order to address this issue properly, it is necessary to have a basic understanding of the chemistry involved. Nitric acid affects anion exchange resins in two ways:

1. attack on the divinylbenzene cross-linkage.
2. attack on the amine functional groups.

Both reactions can occur simultaneously.

Attack of the divinylbenzene crosslinkage, causes a permanent increase in water content and swelling. This reaction is generally fairly slow, occurring over a period of weeks or months. The effect of this type of degradation is that eventually the resin physically breaks down and has to be replaced. The rate of resin oxidation doubles with every 10°C rise in nitric acid temperature [xii]. The resin life can therefore be expected to be 16 times longer at 30°C than at 60°C.

APU systems operating at feed temperatures of less than 32°C have had resin life times of in excess of seven years. On the other hand, laboratory tests showed a 28% swelling factor for an APU resin after continuous immersion in nitric acid at 40-45°C for about a year. While swelling rates of this magnitude would not represent a safety issue, it would necessitate frequent (eg. every few months) disassembly of the unit to remove some swollen resin and regular replacement of the total resin inventory. For immersion at ambient temperatures (ie. 20-25°C) swelling was observed to be less than 2% after the same period of time, which is consistent with field experience.

The consequences of attack on the amine functional group on the resin are potentially much more serious. At a minimum, the capacity of the resin is reduced, but under some circumstance, the reaction between nitric acid and an anion exchange resin can be explosive. This is because a product of the reaction is chemically very similar to ammonium nitrate, a major component of gun powder. Anion exchangers can act as highly unstable explosives and some anion exchange resins in the nitrate form have actually been proposed as rocket fuel [xiii]!

In fact, a number of explosions have occurred where ion exchange resins have been contacted with nitric acid (not with APU's). Following these incidents, several detailed studies were conducted in order to understand the mechanisms involved and to make recommendations on how to avoid them [xiv,xv]. In order for a so-called 'thermal excursion' or explosion to occur, a number of factors come into play. The most significant ones are:

- the concentration of the nitric acid
- the temperature of the nitric acid
- the size (ie. diameter) of the resin bed

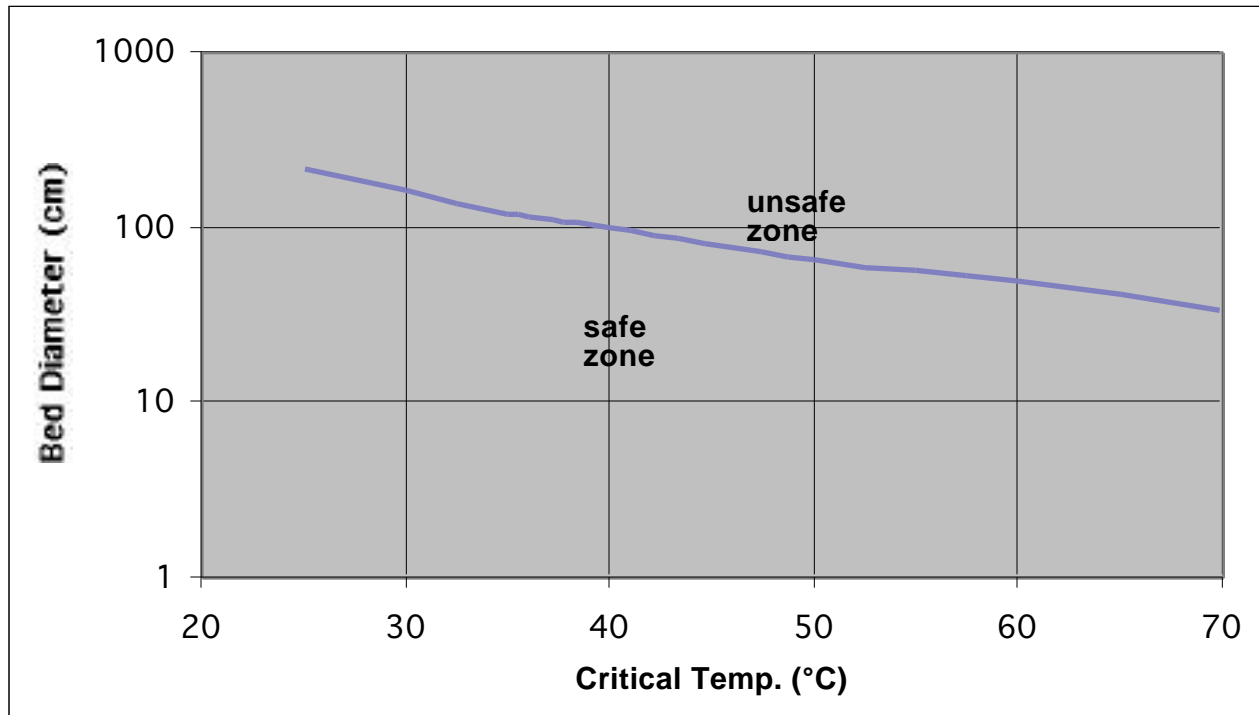
Work conducted by Fullman et al at the Battelle Memorial Institute resulted in a correlation that can estimate the critical nitric acid temperature beyond which there is an explosion risk [xvi]. Based upon a typical mixed acid pickle bath containing 15% nitric acid, the calculated critical acid temperature for various diameter resin beds is shown in Figure 9. Operation below this critical temperature is considered safe.

Given the potentially serious consequences of exceeding the critical temperature, it is essential for most mixed acid stainless steel pickling operations to cool the pickle liquor prior to treatment with an acid retardation system.

### 8. NITRATE FREE FORMULATIONS

Many countries have severe limits on discharge of nitrate to the environment. While operation of an APU will substantially reduce the amount of nitrate discharged from a stainless steel pickling operation, in some cases, strict regulations will necessitate further reductions.

**Figure 9: Maximum Safe Operating Temperature for Acid Retardation Systems**



One alternative is to employ nitrate-free pickling chemistry. There are several nitrate-free formulations available. These typically employ hydrofluoric acid and sulfuric acid and incorporate an oxidant such as hydrogen peroxide. Fortunately, these chemistries are compatible with the APU. To date, three stainless steel mills originally equipped with APU's on nitric/hydrofluoric processes have been converted to nitrate-free chemistry, with excellent APU results.

### 9. FLUOREX™ REGENERATION SYSTEM

A major limitation of the acid retardation technology is that it can only recover free acid values. A significant portion of the hydrofluoric acid that is purchased cannot be recovered since it is lost as metallic fluoride salt. The Fluorex system was developed to recover the total nitrate and fluoride values, including those bound with the metals.

The Fluorex process utilizes sulfuric acid distillation to volatilize nitric and hydrofluoric acid. Unlike previous systems of this type which use crystallization, an APU is employed to remove ferric sulfate and other metal contaminants from the sulfuric acid. Fluoride and nitrate recoveries of greater than 93% and 99% respectively are achieved. The waste from the APU is a mildly acidic solution containing iron, chromium and nickel sulfate which can be neutralized to reclaim the metal values as hydroxides, if desired.

It is worth noting that an APU originally installed as a stand-alone system, (ie. directly on a pickling operation) can be later incorporated into a Fluorex system as part of a retro-fit upgrade. Details of the Fluorex system are available elsewhere [xvii].

#### 4. CONCLUSION

APU acid sorption systems based upon the Recoflo acid retardation technology have been employed by the stainless steel industry for 17 years. Their efficiency and reliability is now widely acknowledged and exploited. The technology has continued to evolve over this period so that today's APU systems are even more efficient than the original technology. In addition, complementary technology is now available to enhance and expand the capabilities of the basic system.

#### REFERENCES

- 
- [i] M.J. Hatch and J. A. Dillon, Industrial and Engineering Chemistry Process Design and Development, vol 2, no.4, 253 (1963).
  - [ii] Brown, C. J. (January 1979). Purification of Sulfuric Acid Anodizing Solutions. Plating and Surface Finishing,
  - [iii] Brown, C. J. (January 1990). Productivity Improvements Through Recovery of Pickle Liquors with the APU Process. Iron and Steel Engineer
  - [iv] Brown, C. J. (1987). Fluid Treatment Process and Apparatus. U.S. Patent, 4673507.
  - [v] Lindroos, K., & Outokumpu, O. (1987). Determination Of Free Hydrofluoric And Nitric Acids In Pickling Bath Liquors Using a Fluoride-selective Electrode and Alkalimetric Titration. Analyst, 112.
  - [vi] Kunin, R. (1976), Safety Practices in Ion Exchange Technology, Amber-Hi-Lites, 153.
  - [vii] Rohm and Haas Company (1976), A Note of Caution of the Use of Nitric Acid with Ion Exchange Resins.
  - [viii] Kuhne, G., Martinola, F. (Bayer AG), Ion Exchangers and their resistance to the effects of chemical and physical factors
  - [ix] J. Sabzali (Purolite Company) (1997), personal communication
  - [x] Mitsubishi Kasei, Diaion Manual of Ion Exchange Resins and Synthetic Adsorbent I (1992), p. 59,73.
  - [xi] Dow Chemical Co., form no. 177-1426-89
  - [xii] Bayer Chemical, Effect of Elevated Operating Temperatures with Strongly Basic Anion Exchange Resins.
  - [xiii] Calmon, C. (1980). Explosion Hazards Of Using Nitric Acid In Ion Exchange Equipment. Chemical Engineering, 3, 271.
  - [xiv] Tichler, P., Baker, L., Isler, R., & Metz, D. (1968). Investigating Committee Report of the Nitrate Resin Bed Accident at the Brookhaven High Flux Beam Reactor. Brookhaven National Library.

- [xv] Van Slyke, W. J., Jansen, G., & Swift, W. H. (1965). Thermal Effects in Anion Exchange Resin Nitric Acid Systems. Battelle N.W. Laboratory, 114.
- [xvi] Fullman, H. T., & Jansen, G. (1970). Thermochemical Instabilities in Anion-Exchange Processing. Ion Exchange in the Process Industry, 71.
- [xvii] Brown, C. J. (1996). The Fluorex Process for Regeneration of Nitric/Hydrofluoric Stainless Steel Pickle Liquors, Presented at the 2<sup>nd</sup> International Symposium on Iron Control in Hydrometallurgy, Ottawa.