Impact of silica on hydrometallurgical and mechanical properties of RIP grade resins for uranium recovery

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Synopsis

Resin-in-pulp (RIP) technology has recently often been considered for the direct recovery of base metals and uranium from dense pulps. Implementation of RIP will eliminate the requirement for any solid-liquid separation downstream of leaching and has the potential to combine the recovery and purification steps, hence reducing both capital and operating costs. The recovery of the valuable metal is expected to be higher when RIP is used, especially where the leached solids are difficult to settle or filter, and to wash.

The main concerns about the use of RIP for uranium recovery from dense pulps are the impact of silica on the resin's metallurgical performance and the operating costs that would be associated with resin loss. Although a number of resin manufacturers have been developing much improved RIP-grade resins, it is critical that the most cost-effective resin be selected. Mintek currently is doing a significant amount of work on silica fouling of RIP-grade strong-base resins in acidic leach liquors and the effect it has on the performance of the resin, including its durability.

This paper describes the results of the test work done on silica fouling and its impact on plant design input data. Resin durability test work was done using various laboratory techniques, but durability was also evaluated on a relatively large scale using actual pumps, screens, and mechanical agitation. Based on the results generated, a preliminary economical evaluation was done to estimate the impact of resin loss on the overall economic viability of a specific application.

Keywords: resin-in-pulp, silica fouling, resin loss, equilibrium, kinetics, elution, durability, mechanical strength, resistance to attrition.

Introduction

Resin-in-pulp (RIP) is being considered by numerous companies for direct recovery of uranium from leached slurries, especially for low grades ores and where solid-liquid separation is difficult and costly. The use of RIP for uranium recovery is not novel—it was quite commonly used, especially in the USA during the 1970s, and it is extensively used in the former Soviet Union. The implementation of this unit operation eliminates solid-liquid separation required after leaching and it has the potential to minimize the recovery and purification steps required, hence reducing both capital and operating costs[1,2].

The primary concerns associated with RIP and ion exchange technologies for uranium recovery from sulphuric acid leached pulps are resin loss and silica fouling. Silica fouling of strong-base resins in acidic leach liquors is a well-known problem on plants using strong-base resins for the recovery of uranium. Silica fouling primarily results in poorer metallurgical performance when compared to fresh resins, but earlier operations found that silica fouling also increased the brittleness of resins once the silica level was allowed to increase above a certain maximum level (for gel-type resins). With the development of improved resins for uranium recovery, the resistance to silica fouling and the impact of silica fouling on the metallurgical and durability performance became important criteria in the choice of the most cost-effective resin.

As part of ongoing development work at Mintek, test work was conducted to evaluate the performances of various gel and macro-porous resins for their suitability to recover uranium from sulphuric acid leach liquors via RIP. It is impractical and very costly to evaluate resin losses on a continuous plant of reasonable scale, and hence various laboratory-scale, accelerated durability tests were used to evaluate the relative durabilities of potential RIP resins. The most promising resins were then also evaluated in the MetRIX™ demonstration plant on site at Mintek.

RIP-grade resins

A number of properties have to be taken into account in the selection of the most appropriate adsorbent for any process. The

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most important of these are matrix, structure, physical form and size, resistance to fouling and osmotic shock, and chemical stability[3,4]. For the recovery of uranium and base metals via RIP, resin stability and strength are probably the most important factors to consider, as it could have a unfavourable outcome on the operating cost of a plant.

The effect of osmotic shock and physical attritioning on resin bead destruction is closely associated with the actual structure of the resin beads. In general, a gel resin is less resistant to the osmotic effects, whereas a macroporous resin shows a lower resistance towards physical attrition. In the case of gel resins, the individual beads assume the form of single compact spheres permeated with micropores (<30 Å). This compact structure, although possessing a high degree of physical strength, is unable to accommodate excessive swelling and shrinkage of the beads during various chemical treatments and the associated changes in the ionic form of the resin, thereby leading to some fracturing of the spheres. The macroporous resin, on the other hand, is made up of a multitude of microspheres within the beads (pore size can vary between 50 and 1 000 000 Å). As a result of the relatively large channels within the bead structure, these bead types are more flexible in accommodating changes in bead volume during chemical treatment, thus reducing the tendency to fracture as a results of osmotic shock. The increased porosity, however, generally reduces the physical strength of the beads and reduces their resistance to physical attrition[3,5].

Smaller beads usually have faster kinetics than larger beads, as the 'path' through which the metal has to diffuse is shorter. However, for RIP applications, larger beads are required. A large difference in the size of the pulp particles and the resin makes the separation of the resin and pulp more feasible. Larger beads generally are physically weaker than smaller beads.

Historically, resin attrition has been an impediment to the extensive introduction of RIP technology into uranium and base metal applications in the Western World. However, a number of resin suppliers now have commercially available resins that are larger and more durable. Mintek is currently creating a comprehensive database of the performances of the available RIP-grade resins for their feasibility to be employed to recover uranium via RIP.

Two types of strong-base polystyrene resins produced by two different suppliers, i.e. gel (GT) and macroporous (MP), were tested during the current investigations. The particle size distribution (PSD) of each of these resins in the sulphate form (pH around 2) is presented in Figure 1. The main ion exchange characteristics as provided by the two suppliers or determined during the test work (i.e. density, d_{50}, etc.) are given in Table I.

MP1 and GT1 resins were bigger in size, exhibited a narrower PSD (uniformity coefficient) and their maximum reversible swelling was lower when compared to MP2 and GT2. These characteristics were advantageous for the resins produced by Supplier 1.

Silica fouling

Silica fouling, a phenomenon observed during the recovery of uranium from sulphuric acid leach liquors using anion exchange resins, results in poorer metallurgical performance and hence metal recovery when compared to fresh resins. With the development and evaluation of new resins for uranium recovery the resistance to silica fouling is an important factor in the choice of an optimum resin[6]. The rate
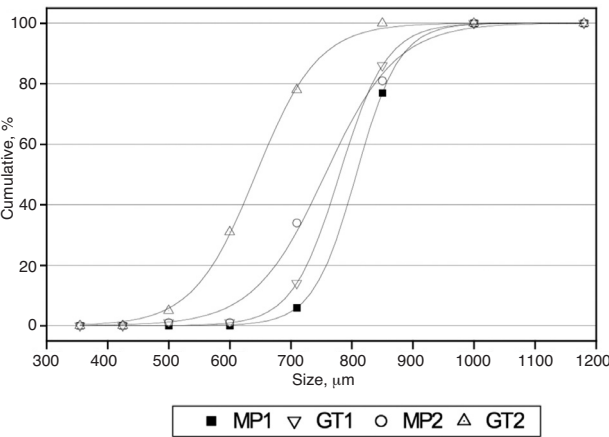

Figure 1—Particle size distributions of various resins in the sulphate form

Table I

Main characteristics of the resins tested (sulphate form)

Resin characteristic	Supplier 1		Supplier 2	
Code name[a]	MP1	GT1	MP2	GT2
d_{50}, µm	807	780	756	643
Uniformity coefficient	0.89	0.88	0.83	0.82
ρ, g/L (based on dry resin, >600 µm)	330 (±1%)	380 (±0.2%)	300 (±1%)	420 (±2%)
Theoretical capacity, eq/L	≥1.15	≥1.3	≥1.0	≥1.4
Moisture retention capacity,%	53–58	40–50	48–60	40–47
Max reversible swelling Cl⁻→OH⁻,%	15	20	20	30
Matrix	Macroporous	Gel	Macroporous	Gel

[a]Code names were used for the various resins to simplify discussion

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of silica fouling depends on various parameters including composition of the leach liquor (silica content and other elements background), pH, temperature, and residence time in the pulp.

Decreases in loading and elution rates with 'fouled resin' when compared to fresh resin result in longer residence times being required in both the adsorption and elution circuits to recover the same amount of uranium. Furthermore, the longer the residence time in the adsorption circuit, the higher the silica loading and hence fouling problem.

During the current investigations it was established that analysis of silica loading by stripping of a portion of the loaded resin with NaOH and analysing the strip liquor or eluate is a more accurate method than direct resin analysis, and gave better overall accountabilities. Moreover, it would be easier to perform silica analysis on the plant using this procedure than via direct analysis of the resin. Analysis of the NaOH-stripped resin gave residual silica contents near the detection limit of inductively coupled plasma-optical emission spectroscopy (ICP-OES) of 0.05%. Silica loadings are expressed as percent of SiO_2 per gram of fresh resin, for the reason that during plant operation the resin in operation will change density due to loading of various metals including uranium and silica.

Resins prefouling with silica

Synthetic silica fouling tests were done on the two gel and two macroporous resins being investigated in order to obtain an indication of their silica fouling rates and provide silica-containing samples for subsequent durability and hydrometallurgical test work.

A portion of resin in the sulphate form was contacted with a freshly-prepared 3 g/L of SiO_2 solution (using sodium silicate) during 24 hours in rolling bottles at pH 1. The solution-to-resin volumetric ratio was 10 to 1. At the end of the first cycle of fouling, the resin was washed with de-ionized water to remove entrained solution and a portion of the resin was removed for further test work and analysis of loaded SiO_2. The remainder of the resin was subjected to the next cycle of fouling using a similar procedure as described for the first cycle. A total of 4 cycles (for GT2 3) of fouling were conducted this way. Results are presented in Figure 2.
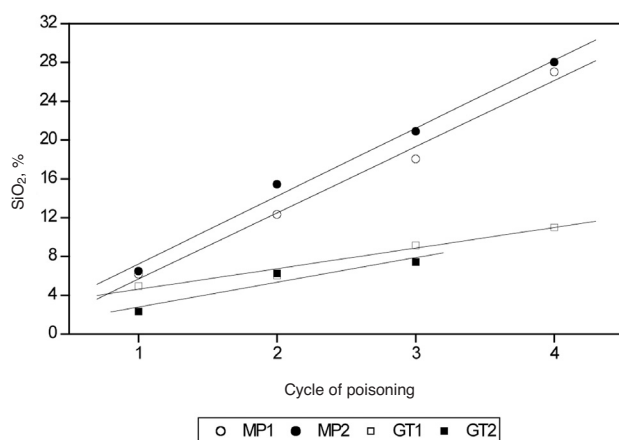

Figure 2—Resin fouling with silica in synthetic fouling tests

Silica loading rates of the two macroporous resins, under the conditions used during this test work, were very similar, as were those of the gel-type resins. The macroporous-type resins loaded silica at a higher rate than the gel-type resins. The silica-fouled resins were submitted to scanning electron microscopy (SEM), abrasion and hydrometallurgical performance tests.

SEM of silica-fouled resins

Silica-fouled resins were analysed by SEM to establish the silica distribution inside the resin sphere. Five samples of each resin (excl. GT2) were analysed by SEM, namely fresh resin in the sulphate form, and silica-fouled resin after each cycle of fouling.

A portion of each of the resin samples was mounted individually in epoxy resin. After hardening of the resin, the disk was carefully sliced through the centre of the resin spheres and then polished. The polished area was carbon coated to make it conductive for observation on the Jeol 840A SEM. Backscattered-electron imaging (BEI) and energy-dispersive X-ray spectrometry (EDS) were employed to obtain the requisite data from the sections.

An image of a suitable resin sphere was taken and a line scan analysis performed across the sphere. In this case, a 10 second EDS analysis was gathered at each of 50 evenly spaced intervals along the line, across a resin sphere. The X-ray counts for silicon at each point were recorded.

Results of SEM, BEI and EDS are summarized and graphically presented in Figure 3. The profiles of silica fouling was different for gel and macroporous resins. For GT1 the silica primarily concentrated on the rims of the resin, with a sharp dropp-off in the silica concentration towards the centre of the bead. GT2 contained no silica in the centre of the bead.

For the macroporous resins, MP1 and MP2, the silica initially also concentrated primarily on the rims of the resin, but a broader band of silica was observed and hence the increase in silica concentration penetrated somewhat deeper into the resin. At significantly higher silica content (27–28%) on the resin, the silica concentration towards the centre of the bead also increased significantly. This difference in behaviour when compared to gel-type resins most probably explains the fact that the hydrometallurgical performance of gel-type resins are more adversely affected by the silica content on the resin[5,6]. It appears that the silica formed a film around the gel-type resin beads, which retarded diffusion into and through the micorpores. On the other hand, the silica films also formed on the macropores of the macroporous resins, causing a higher rate of silica fouling due to the higher surface area available. Nevertheless, the higher surface area still provided a higher surface for diffusion to take place.

Impact of silica fouling on hydrometallurgical performance

Adsorption

Adsorption equilibrium isotherms were established for the loading of uranium onto fresh and silica-fouled resins (various extents of silica) in the sulphate form, by batch

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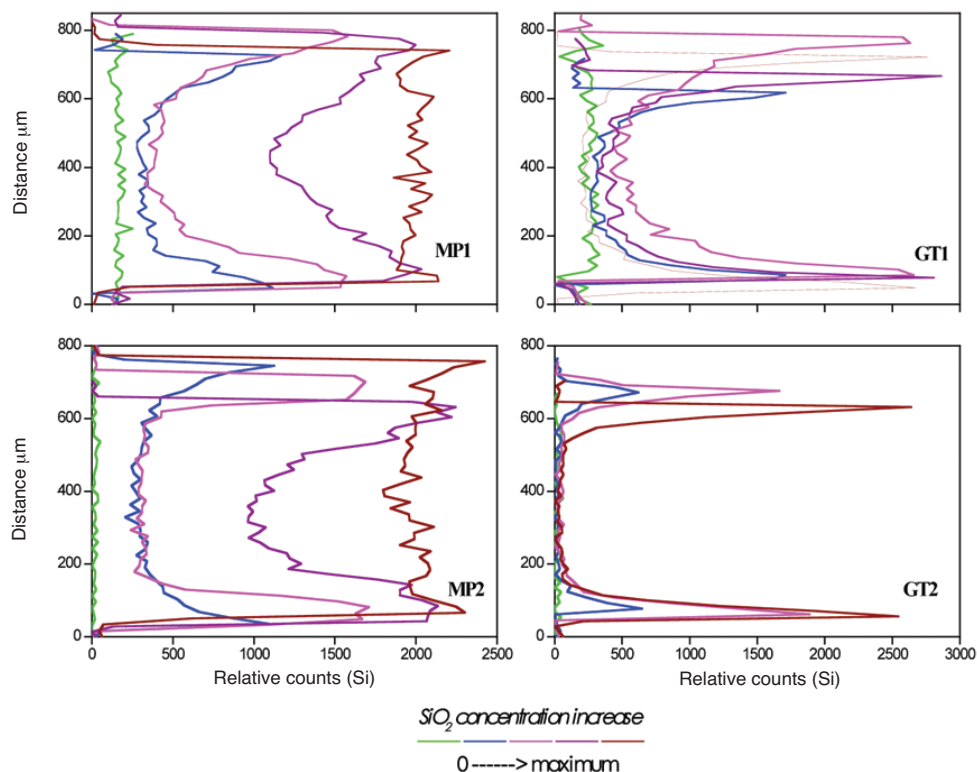

Figure 3—Results of SEM, BEI and EDS of silica fouled resins

contacting portions of the resin and synthetic solution (220 mg/L U_3O_8, 1 g/L Fe^{3+} and 20 g/L SO_4^{2-} pH 1.8) at different resin:solution volumetric ratios. The resin and solution were contacted at ambient temperature in rolling bottles for a period of 24 hours.

Relative losses in the maximum uranium loadings versus silica contents on the resins are shown in Figure 4 (maximum uranium loading capacities were taken at 200 mg/L barren U_3O_8 concentrations). Decreases of uranium loading capacities (over 24 hours) were observed, especially at the higher silica levels. GT2 resin, with the smallest bead size, was most seriously affected by silica. At 6% SiO_2 on the resin more than 50% of uranium loading capacity was lost.

Equilibrium loading results (Figure 7) confirmed that the impact of silica on the loading performance of gel-type resins is more severe than on macroporous resins. However, the rates of silica loading onto the macroporous resins are higher due to higher permeability of the beads. Thus, an evaluation to determine the most cost-effective resin option would be rather complex.

Adsorption kinetics

Kinetic tests were conducted to evaluate the rate of uranium loading from a synthetic solution onto the MP1 and GT1 resins. These resins were chosen to eliminate the impact of resin size on the rate of uranium loading (d_{50} values of GT1 and MP1 resins were very similar, Figure 1) and to consider only the effect of silica on the rate of loading.

Kinetic tests were performed by contacting a portion of the fresh or silica-fouled resin in batch with the synthetic solution in a baffled, stirred reactor for a total period of 24 hours at ambient temperature. Fractional uptake of uranium

(characterizes approach to equilibrium) versus adsorption time is shown in Figure 5.

The kinetics of the gel type resin was initially faster than that of the macroporous resin. 100% uptake was achieved within less than 8 hours for GT1, when MP1 resin recovered only 90% of U_3O_8. The decrease of the fractional uptake after 8 hours of contact versus silica content of the resin (Figure 8) indicated that the impact of silica on the rate of loading of the gel type resin was more severe when compared to the macroporous resin when the silica level on the gel resin increased above 10%. The loss of fractional uptake versus silica content for MP1 resin was linear, with around 0.8% decrease in the fractional uptake (over 8 hours) per every
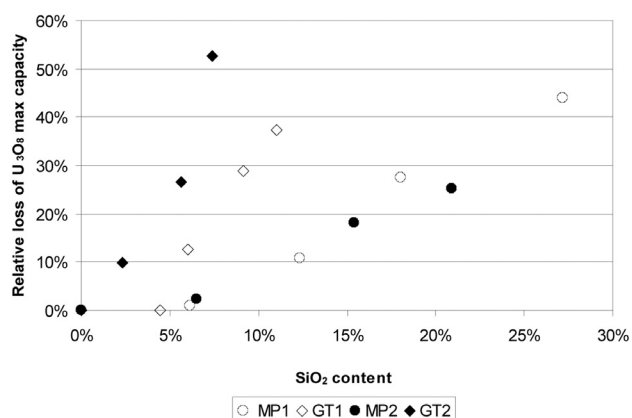

Figure 4—Effect of silica on the maximum uranium loading capacity of the resins over 24 hours

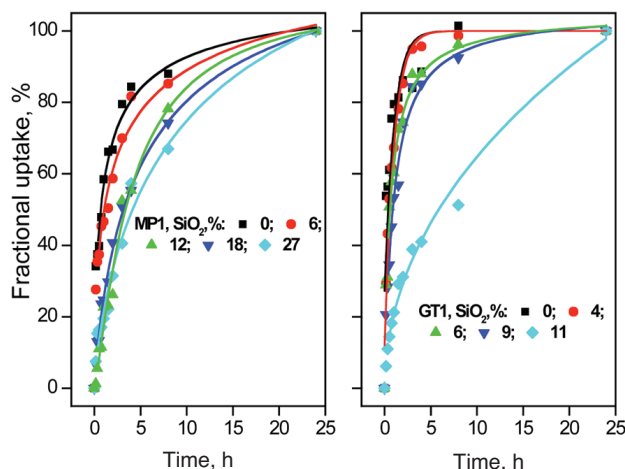# Impact of silica on hydrometallurgical and mechanical properties

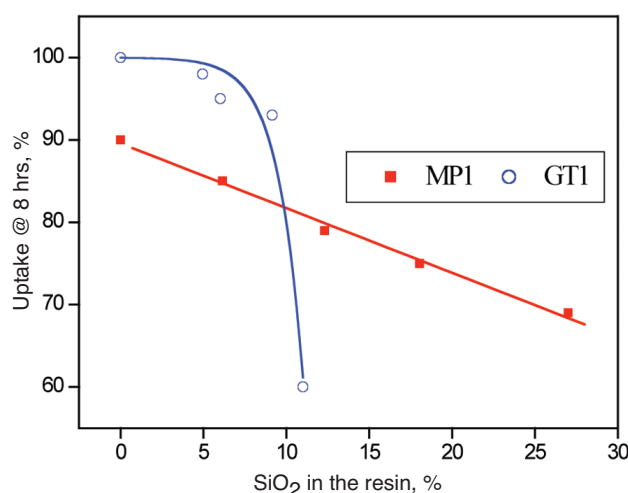**Figure 5—Fractional uptake of uranium versus time (approach to equilibrium)**

Figure 6—Impact of silica content on kinetics of uranium adsorption

additional 1% of silica reporting to the resin. A similar loss in uptake per % silica increase on the resin was observed for the GT1 resin up to about 10%, whereafter there was a sharp decrease in performance.

It is obvious that silica fouling and a decision on the bleed stream (for caustic regeneration) silica concentration should be seriously considered from the beginning of uranium sulphuric acid leach plant design. The rate of silica build-up should be evaluated at an early stage.

Effect of silica on adsorption performance

McCabe-Thiele constructions were done on equilibrium adsorption isotherms generated for gel (GT1) and macroporous (MP1) resins to get an indication of the impact that silica would have on the number of stages required for efficient uranium recovery at fixed resin/pulp ratios. Resins with no silica and silica-fouled resins were studied and results are presented in Figure 7. In all the cases all the cases kinetics aspects were taken into the account, extraction efficiency was taken from kinetics results after 8 hours of contact.

Results confirmed that the level of silica fouling on the resin is critical for its metallurgical performance and should be taken into account during test work so that more realistic design parameters could be generated. Silica decreases not only the maximum uranium loadings over reasonable resin residence times, but it also increases the number of stages, resin inventory, and resin flowrate to achieve a recovery of below 2 mg/L in the barren.

Test work required for generation of plant design parameters should be done using the resin containing the silica level that would be targeted for the full scale operation. The silica level would be controlled at this level via NaOH regeneration.

Uranium stripping isotherms

Silica-fouled resins (MP1 with 15% and GT1 with 9% of SiO_2 fouling) were preloaded with uranium from an actual pulp containing 161 mg/L U_3O_8, 721 mg/L SiO_2, 2 g/L Mn and 3.6 g/L Fe at pH 1.8. Loadings of 30 g/L U_3O_8 were achieved for both resins. Preloaded resins were used for uranium stripping equilibrium and kinetic test work. The samples were contacted in different resin/eluate ratios over a period of 10 hours (in batch) with 80 g/L H_2SO_4 at ambient temperature. Thereafter the resin and solutions were separated and the eluates were analysed for uranium and acid. The stripped resin samples were re-stripped consecutively with HNO_3 and NaOH to efficiently strip the remainder of the uranium and silica respectively. Eluates were analysed for their uranium and silica contents.

Equilibrium stripping isotherms generated for macroporous and gel type resins using 80 g/L H_2SO_4 as eluant are presented in Figure 8, and the residual acid concentration in the eluates versus uranium content is shown in Figure 9.

Stripping isotherms obtained were quite flat or linear, indicating that the stripping is relatively unfavourable. The gel resin stripping isotherm was more favourable than that of
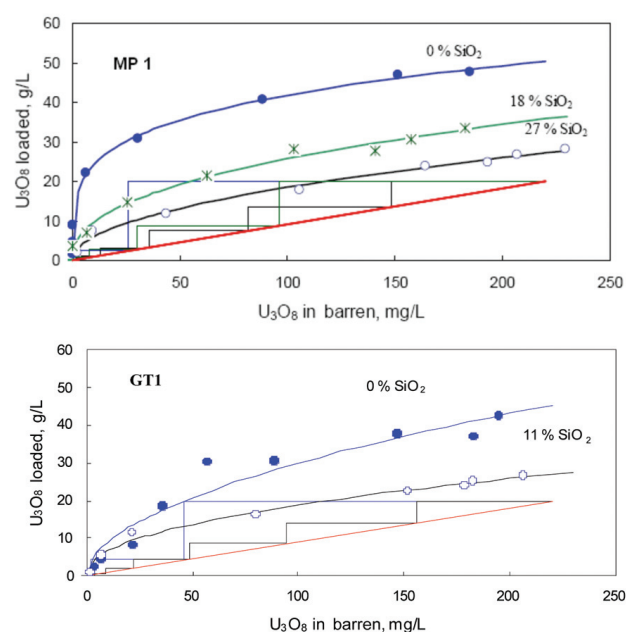

Figure 7—Impact of silica fouling on number of stages

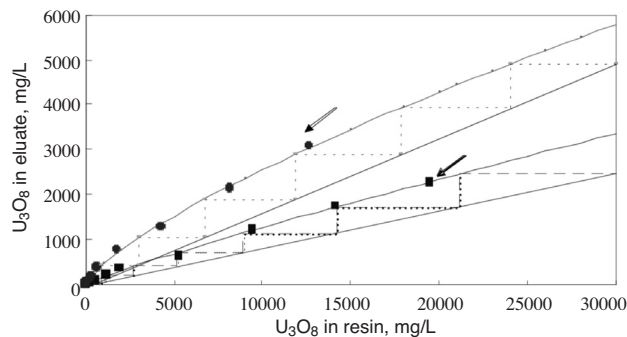# Impact of silica on hydrometallurgical and mechanical properties

Figure 8—Uranium stripping isotherms

GT1: $y = -0.0056x + 80.272$
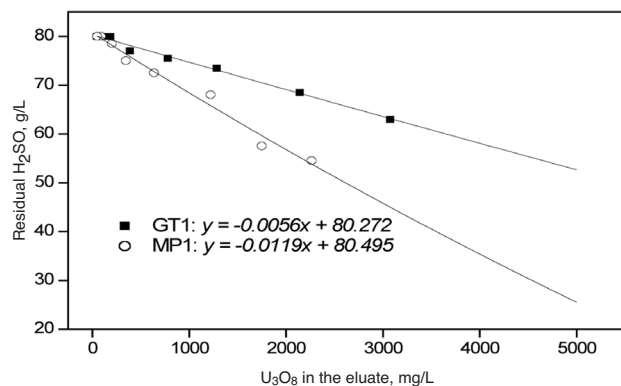MP1: $y = -0.0119x + 80.495$

Figure 9—Residual acid concentrations: uranium stripping isotherms

the macroporous resin. Higher acid concentrations should be used to make the stripping somewhat more favourable, but these results clearly indicate that stripping of uranium from a strong-base resin could be equilibrium constrained if too low eluant flow rates and total volume are applied. This also indicates that in order to produce relatively high uranium concentrations in the eluate, continuous countercurrent elution would be the most efficient approach.

Residual or barren H_2SO_4 concentrations, after equilibration with the uranium loaded resin, was lower for the macroporous resin than the gel resin. This was surprising in that the resins had similar uranium loadings, and the gel resin has a higher theoretical capacity. It might be that the sulphate/bisulphate behaviour inside the resins were different during this test work. The effect of acid concentration and potentially other eluates on stripping efficiency is currently under investigation.

Kinetics of stripping

Kinetic stripping tests were conducted to evaluate the rate of uranium stripping from the resins using 110 g/L H_2SO_4 as eluant at ambient temperature. MP1 and GT1 resins fouled with silica to 15 and 9% of SiO_2 respectively and loaded with 30 g/L of uranium were contacted with 110 g/L of H_2SO_4 at a solution/resin ratio of 60 under vigorous agitation at ambient temperature in a baffled reactor. Fractional stripping of uranium from MP1 and GT1 resins is presented in Figure 10.

The rate of stripping of the gel resin was slightly slower compared to that of the macroporous resin. Uranium desorption was completed in less than four hours. The

relatively fast kinetics of uranium stripping indicated that often the total volume of eluant, and not elution time, could be the constraining factor for efficient uranium stripping of uranium from strong-base ion exchangers.

Impact of silica on resin abrasion and durability

Generally, the preferred resin for a RIP application would not be the product that achieves the highest uranium loading only, but it would be the product that better conforms to the various requirements of the RIP process. Particle size and physical strength or durability of the resin are two of the most important considerations in this regard. The resin should be strong enough to withstand degradation as a result of osmotic shock in the varying chemical environments during loading and elution cycles, as well as the harsh physical environment of a well-mixed, dense slurry and resin handling (screens, pumps, etc.).

As it is impractical to evaluate resin losses on a continuous plant of a reasonable scale, accelerated durability tests were developed to evaluate the relative abrasion and durability of various resins. Resin abrasion tests were done in the laboratory using sand and a dense pulp medium. The breakdown or loss of resins per cycle is represented as the percentage volume decrease during a cycle (i.e. based on the volume of resin at the beginning of that specific cycle). Volume measurements were taken on resins in the sulphate form.

Denver flotation cell in presence of silica sand

The influence of silica content and NaOH treatment on the abrasion resistance of gel and macroporous resins was tested. The primary objective of these tests was to establish the relative breakdown rates of RIP-grade resins by subjecting them to a relatively standard accelerated durability test procedure. This approach only provides information about the relative abrasion resistance of resins, and does not provide any information about predicted resin losses for a full-scale operation.

Only fresh resins (without silica) were used to determine the influence of NaOH treatment (large pH swing) on the abrasion and durability of the resins. Tests started with
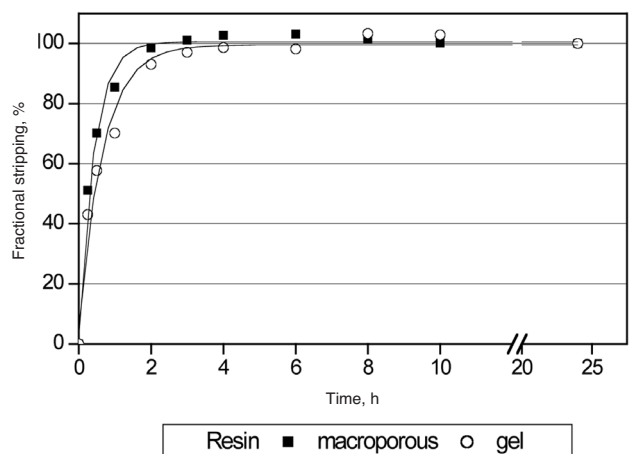

Figure 10—Kinetics of uranium stripping

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200 mℓ of resin in the sulphate form, and resins were pre-screened to eliminate beads smaller than 600 μm. Excess water was removed. The resin was transferred to the Denver flotation cell (2000 L 16 × 16 cm) with 1400 mℓ deionized water. The agitator assembly consisted of an impeller housing ($\emptyset$ = 11 cm, tooth 12 × 8 mm) and impeller ($\emptyset$ = 10 cm, blade 30 × 7 mm). Graded sand (75–212 μm; 725 g) was added. The resin and sand were agitated in the flotation cell for 60 minutes at 1500 rpm. The sand was washed away with deionized water, and the wet-settled resin fraction > 300 μm was screened and measured, and the PSD determined. The resin fraction greater than 300 μm in diameter was mixed and transferred into a clear perspex column for osmotic shock treatment using the conditions listed in Table II. The physical/chemical treatment was repeated 5 times (5 cycles).

Fresh and silica-fouled resins were subjected to this procedure, but the NaOH/water treatment of the silica-fouled resins was excluded from the chemical treatment step as NaOH would strip silica off the resin. Thus only the acid treatment step was used to represent osmotic shock for the silica-fouled resins. The sand-water mixture was prepared using pH 2 water to eliminate silica stripping from the resin. The resin loss per cycle was calculated taking into account fractions bigger than 600 μm.

The resin loss per cycle of physical/chemical treatment had a linear character and average loss per cycle of aggressive attritioning versus silica content in the resin is shown in Figure 11.

Table II
Osmotic shock procedure

Reagent	Concentration g/L	Duration min	Flow rate mℓ/min	Volume mℓ
NaOH	80	30	20	600
H_2O	-	30	50	1500
H_2SO_4	200	30	20	600
H_2O	-	-	50	to pH 2
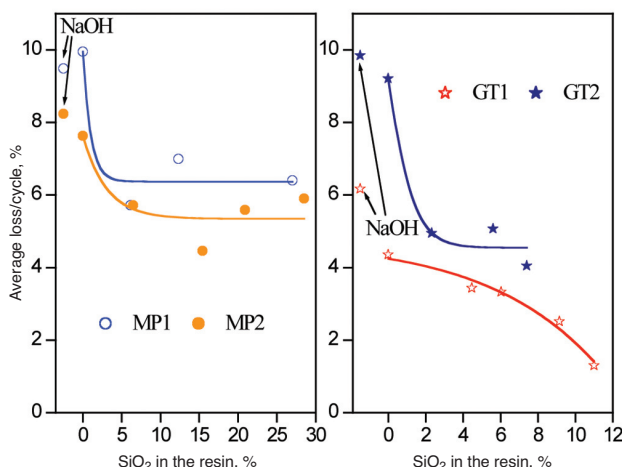
Figure 11—Influence of different silica levels and NaOH treatment on resistance of resins to aggressive attritioning

NaOH treatment caused the resins to weaken, especially in the case of gel-type resins. The performance of MP1 showed no or very little change when treated with caustic. Hence, the impact of NaOH treatment on the full-scale plant during regeneration of this resin is expected to be limited.

Silica fouling of the resins to the levels tested resulted in some improvement of their resistance to attrition compared to the 'fresh' resins. In the case of macroporous ion exchangers the resistance to attritioning increased by around 2–3%. Although results indicated that the resins exhibited an increased resistance to attrition at the silica levels tested, the trend is expected to reverse at higher levels of silica on the resin.

Stirred reactor using dense pulp medium

In the past generally only gel-type resins were considered for uranium recovery, as the rate of silica fouling of macroporous resins was significantly higher. However, since then some work done by Rohm and Haas indicated that although macroporous resins fouled faster, the impact of silica on the resin's metallurgical performance was less[7]. Hence, only macroporous-type resins were tested in the laboratory for their resistance to attritioning using unleached uranium pulp.

Resins MP1 and MP2, fouled with silica to different extents, were subjected to 5 cycles of physical and chemical (osmotic) shock treatments and the percentage of resin loss per cycle was determined. Physical treatment of the resins consisted of aggressive agitation at 1140 rpm over 4 hours in a 50% (m/m) solids slurry and a resin concentration of 10% (v/v). Pulp was prepared by mixing uranium-containing milled ore (< 150 μm) with distilled water to prevent uranium leaching, as uranium leaching and loading would have complicated the way in which the test work could be done due to legislative regulations. Resin in the sulphate form, prescreened to > 600 μm, was used. After physical treatment or shock, the resins were treated in a column with 110 g/L H_2SO_4 at 4 bed volumes per hour (BV/h) over 1 hour, followed by a wash cycle with distilled water to about pH 2. Particle size distribution (PSD) of each of the resins was determined after 5 cycles of abrasion. Volume measurements were done on resin in the sulphate form and the average loss per cycle of attritioning and the d_{50} versus silica content on the resins are shown in Figure 12.

Variations observed during the accelerated durability tests of the MP1 resin, fouled with silica to different extents, were relatively small. The average resin loss per cycle, irrespective of silica loading, was 10–11% and the total loss after 5 cycles of attrition was on average 54%. A similar behaviour of the MP2 resin to sand attritioning test work was observed. Silica caused some improvements of resin resistance to attrition. Decrease of d_{50} after durability test indicates that abrasion of the resin by the fine particles of the pulp/sand occurred.

MetRIX™ demonstration durability trial

Mintek and Bateman designed and constructed a MetRIX™ (Metal Recovery through Ion-eXchange) RIP modular, demonstration plant under a collaboration agreement. The plant was built and commissioned on site at Mintek. The plant is used to demonstrate the potential of RIP and to

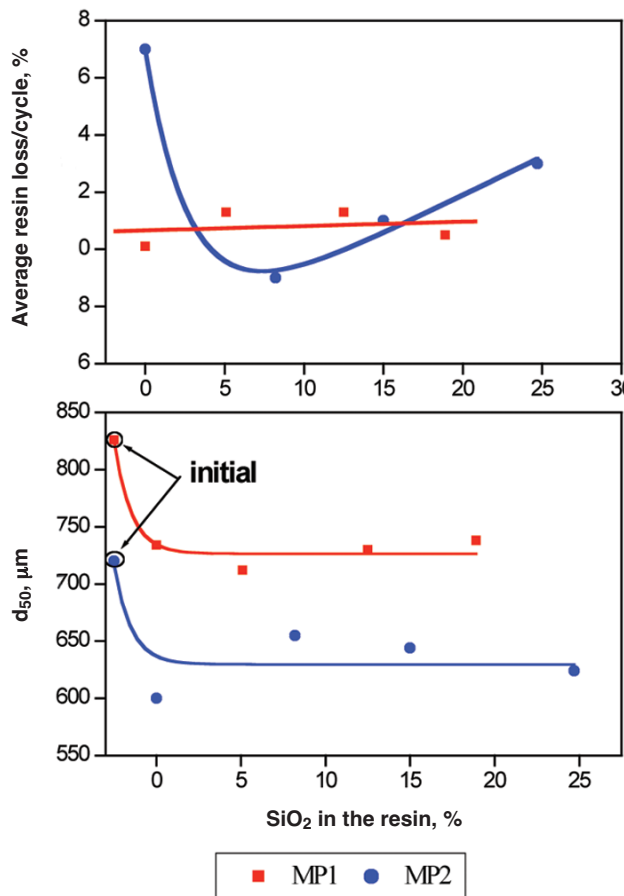# Impact of silica on hydrometallurgical and mechanical properties

Figure 12—Influence of different silica levels on resistance of resins to attrition with pulp

enable prospective clients to test aspects of the technology on site or to move the plant to an operating site for test work. The modular skid-mounted MetRIX™ demonstration plant consists of four adsorption stages of 2 m³ each and an elution circuit.

Durability of two RIP-grade macroporous resins and a gel resin prefouled with silica up to 12–15% and 7% respectively (using a similar procedure as described earlier) was evaluated using the MetRIX™ technology. The resins were passed through the same cycles of adsorption and elution during the durability trial. A flow diagram is shown in Figure 13. Table III provides the operating parameters of the plant.

The 'adsorption stage' involved agitation of the resin in the tank, while the resin was pumped over the sieve bed screen at the estimated required flow rate. The screen overflow (resin) and underflow (pulp) were allowed to return to adsorption stage during this period. This 'adsorption stage' lasted for three hours. After three hours the resin transfer stage started. The overflow (resin) from the screen was shifted to a storage tank for 2 hours, which removed approximately 55% of the resin from the adsorption stage. The remainder of the resin and pulp were pumped out mechanically over the next 2–3 hours, and the resin was screened out. The underflow from the screen (pulp) was pumped to the feed tank, which acted as a holding tank until the next 'adsorption stage' started. The resin in the storage tank was

then transferred to the elution column where it was fluidized and subjected to 100 g/L H_2SO_4 acid treatment (representing elution). This process constituted one cycle and 6–8 cycles were performed per week. At the end of each week the resin was transferred into a graduated column, which was fluidized to determine the free wet settled volume. Some silica was stripped from the resin after 2 weeks of operation and additional fouling had to be done.

The most significant results generated during the MeTRIX™ durability campaigns are presented in Table IV and Figure 14.
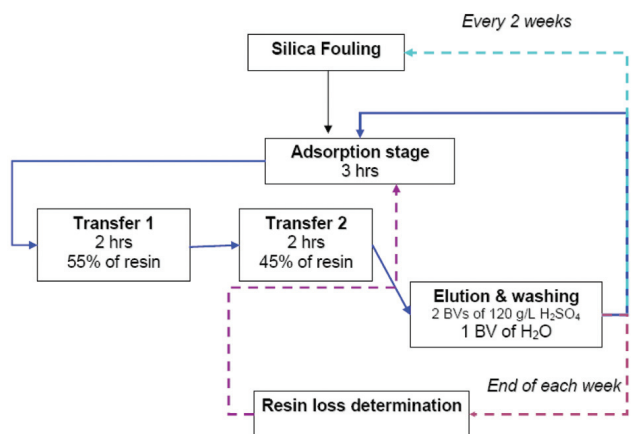

Figure 13—Durability test work in MetRIX™ demonstration plant

Table III		
Operating conditions for MeTRIX™ RIP durability trial		
Pulp		
Pulp density	1.46	kg/L
Residence time	0.50	h
Flow rate	4.60	m³/h
Mass flow rate pulp	6.72	t/h
Mass flow rate solids (50% m/m solids)	3.36	t/h
Solution flow rate (density of 1 kg/L)	3.36	m³/h
Resin		
Resin flow rate	86	L/h
Resin residence time/stage*	1.3	h
Concentration	4.8	%
Resin volume	110	L

*Limitation of pump. Should be 1 h

Table IV			
Results of resin durability trial			
Parameter	Resin		
	MP1	MP2	GT1
Duration of run, weeks	5	3	3
Change in resin volume (initial – final, L)	0	10	2
Number of cycles	34	21	19
Days of operation[a]	46	28	26

[a]Assuming a 36-hour cycle on an operating plant and 90% plant availability

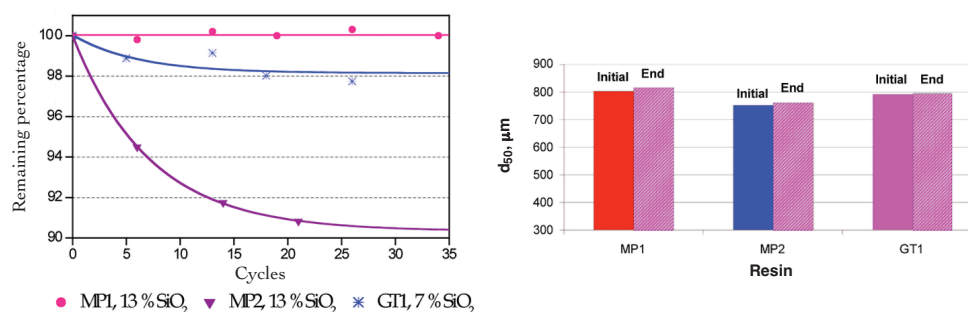# Impact of silica on hydrometallurgical and mechanical properties
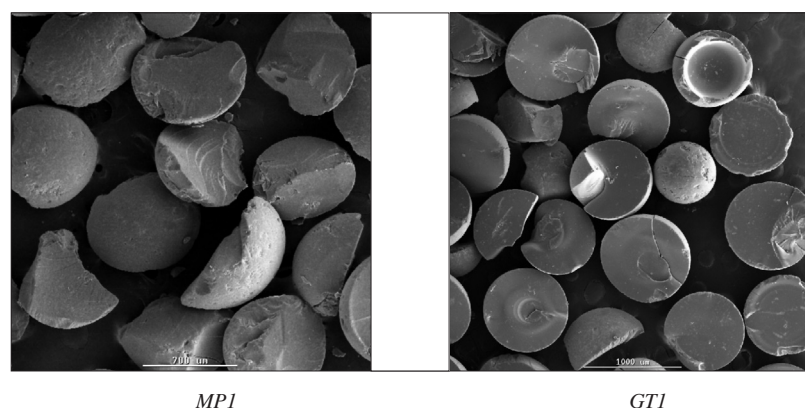
Figure 14—Resin loss and d_{50} during MetRIX™ trial

MP1   GT1

Figure 15—Broken resin beads in + 600 μm fraction

The highest resin loss was observed in the first week of operation and then levelled out for MP2 and GT1 resins. In the case of MP1 no loss was observed after 5 weeks of operations. Particle size distribution remained constant during the trial, which indicated that resin loss on the RIP plant occurred due to percussive action (pumping, screening, resin handling, etc.) and no or very little abrasion.

The optical imaging of the broken resin beads of MP1 and GT1 resins are shown in Figure 15. Although no resin loss was measured for the MP1 resin, a small quantity of broken beads was also recovered from the pulp during evaluation of this resin. These broken beads, however, were still larger than 600 μm and hence retained on the screen. Closer investigation indicated that most of the resin was broken and very little or no resin 'peeling' was observed.

The data obtained with the MetRIX™ demonstration plant appear to be somewhat different from those obtained during the laboratory attrition tests. The laboratory results indicated that GT1 and MP2 was somewhat more resistant to attritioning than MP1, whereas the MetRIX™ results suggested that lower operating losses could be expected for the MP1 resin. Based on this information it was decided that a further test method on tensile strength and resin resistance to mechanical impact (ball mill test) will be added to the laboratory methods of resin evaluation.

Resin loss comparison to some gold RIP operating data

Operational losses for the Minix and Duolite A161 RIP resins were previously reported as <5 g/t for the Penjom[8] and <10 g/t for the Golden Jubilee[9] RIP plants respectively. These are both strong-base resins, and although the Minix gold selective resin has a different structure and composition from the current strong-base resins considered for uranium, the Duloite A161 RIP resin is very similar. These two resins were therefore included in the accelerated degradation test work as described below (abrasion with sand followed by NaOH-H_2SO_4 treatment). Cumulative resin loss per cycle of the physical/chemical treatment is presented in Figure 16.

The Minix resin was by far the most robust. The closest resin to Minix was GT1. The behaviour of the A161 RIP resin was quite similar to that of the macroporous resins in these tests. Although the gold plant results might not give an accurate reflection of potential resin losses on a uranium RIP plant, it probably is a reasonable indication of what the full scale resin loss would be considering the results obtained in the MetRIX tests.

Effect of resin breakage on OPEX

Based on the MetRIX™ durability results and the known operating resin losses for two gold resins, operating losses for MP1, MP2 and GT1 were estimated. The conditions shown in Table V were chosen to evaluate the contribution of resin breakage to operating costs for a specific application. Data used in this comparison are derived from a model developed by Bateman and Mintek, which estimates the operating costs of the chosen flowsheets based on various supplied parameters. The model was run using parameters typical of Witwatersrand gold ore-based slurries, using a range of values for RIP resin breakage.

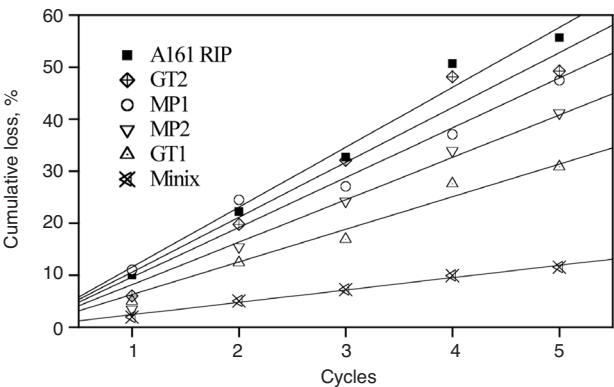# Impact of silica on hydrometallurgical and mechanical properties

Figure 16—Comparison of resistance to attrition between new RIP-grade size resins, Minix and Duolite A161 RIP

Table V	
Conditions for OPEX evaluation	
Uranium production:	100 kg/h U_3O_8
Leached slurry concentration:	200 mg/L U_3O_8
RIP flow sheet:	MeRIX™ based RIP followed by SX using Bateman pulsed columns
Reference flow sheet:	CCD followed by SX using Bateman pulsed columns

At the rates of resin breakage measured, the contribution of resin replacement cost to the operating cost of the plant are estimated to be between 0.08 USD and 0.38 USD per pound of uranium produced for the resins tested. To place these values in perspective, the total operating cost of a typical South African uranium plant, treating this type of ore, would be in the region of 20–30 USD/lb.

The resin replacement cost calculated above is of a similar order of magnitude to the estimated expenditure on reagents for a conventional uranium plant such as flotation reagents or SX plant organics. To illustrate this, the cost of annual RIP resin replacement is plotted at various breakage rates in Figure 17.

The cost of the two major reagents in the CCD-SX flowsheet, flocculent usage and replacing organic losses for the equivalent plant, are plotted on the same graph. It can be seen that the annual resin cost only matches the cost of major reagents in a conventional plant at rates of resin breakage far higher than those measured in MetRIX™ test work programme. Although these high rates were not achieved during test work on the MetRIX™ plant, it should be noted that higher silica loadings on the resin than those tested during this test work programme may result in resin embrittlement and consequently higher resin breakage. Moreover, caustic treatment required to regenerate silica-fouled resin was excluded during the durability trials. Resin degradation is unlikely to influence the economic viability of uranium projects significantly (if SiO_2 fouling is handled appropriately). However, major cost savings can be achieved by selecting the correct resin for the application and having an optimum plant design, such as the MetRIX™ technology, that minimize the impact of resin handling. Efficient management of the plant operation also minimizes resin loss.

Conclusions

A test work programme to determine hydrometallurgical and mechanical characteristics of RIP-grade resins currently available on the South African market was initiated at Mintek. Investigations were done to evaluate the effect of silica fouling on the performance of currently commercially available RIP-grade strong-base resins. Two types of resins, namely, gel and macroporous, provided by two different suppliers were tested. The most significant results of the test work to evaluate the impact of different silica-fouling levels on the chemical (hydrometallurgical) and physical performance of the resins were as follows:

➤ SEM scan of the resins indicated that silica concentration in the gel resin increases mainly on the edges of the resin beads and the penetration was quite shallow, while for macroporous resins the silica also appeared primarily on the rims, but it penetrated deeper into the resin. At relatively high silica levels on the macroporous resin (>10%), the silica levels increased towards the centre of the resin as well. The intensity of the silica signals on the edges of the macroporous and gel type resins where almost the same at 18 and 9% of SiO_2 levels respectively.

➤ Silica fouling of the macroporous and gel type resins to 25–28% and 5–11% respectively (depending on manufacturer) caused more than 40% decrease in maximum uranium loading over a period of 24 hours.

➤ Rate of uranium loading for macroporous resins decreased linearly with silica content increase. Rate of loading by gel type resins of similar size also decreased linearly in the beginning of silica build-up and after ~10% SiO_2 a sharp decrease was observed.

➤ During plant design, the impact of silica on equilibrium and kinetics of adsorption has to be taken into account in order not to under design the plant; the number of stages and resin/pulp ratios increase significantly with silica build-up.

➤ Kinetics of uranium elution was similar for both resins tested, and uranium desorption was completed in less than 4 hours.

➤ Stripping isotherms obtained for gel and macroporous type resins were quite flat or almost linear. These relatively unfavourable stripping isotherms indicate that the elution system needs careful design to prevent equilibrium constraints during stripping of strong-base resins using sulphuric acid as eluant.
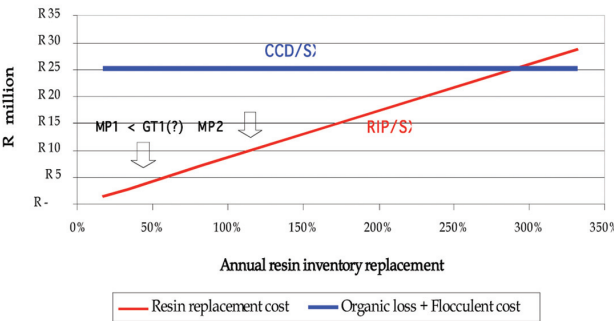

Figure 17—Cost of resin replacement

Impact of silica on hydrometallurgical and mechanical properties

➤ The stripping isotherm of the gel-type resin was more favourable than that of the macroporous resins, while the residual acid concentration was lower for the macroporous resin.

➤ Sodium hydroxide treatment resulted in weakening of primarily gel-type resins. Weakening of the resins occurs due to swelling/shrinking of the resin during sequential chemical treatments, which has a bigger impact on gel resins. The macroporous resins were less susceptible to weakening during NaOH treatment, especially the MP1 resin.

➤ Silica fouling of the resins to the levels tested resulted in a slight improvement to their resistance to attrition compared to the 'fresh' resins tested.

➤ Accelerated attritioning results indicated that the new gel resin, GT1 (big size, d_{50} = 780 μm), performed well in the attrition tests as well as the MetRIX™ demonstration plant.

➤ Laboratory results obtained with the macroporous resins were somewhat different from these determined using the MetRIX™ demonstration plant, presumably indicating different contributions of abrasive and percussive forces applied to the resin beads during the tests conducted.

➤ Modelling of the impact of resin loss on the OPEX of a uranium RIP plant indicated that the annual resin loss cost only matches the cost of major reagents in a conventional plant at degradation rates far higher than those predicted from the MetRIX™ demonstration trials.

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