

RECOVERY OF URANIUM FROM DENSE SLURRIES VIA RESIN-IN-PULP

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ABSTRACT

The revival of uranium as a valued commodity has prompted a drive in the mining industry to identify the most cost-effective processing routes for the recovery of uranium from low-grade uranium ores or wastes. Various published studies indicated that direct recovery of uranium from the leached slurry via resin-in-pulp offers major capital and operating cost advantages. Mintek, in partnership with Bateman Engineering, developed the MetRIX™ RIP technology that allows continuous counter-current transfer of resin and pulp. Laboratory and pilot plant test work was done on uranium recovery from a South African gold ore. Based on these results, operating parameters were developed for a demonstration plant on site at the Harmony's One Plant near Welkom in the Free State for the recovery of uranium from their current gold plant feed prior to cyanidation. This paper summarises the metallurgical results obtained during various laboratory studies, a pilot plant campaign, and the on-site demonstration plant operation.

1. INTRODUCTION

During the 1970s the demand for uranium had catapulted, resulting in renewed interest for processing routes that were cost-effective for the recovery of uranium from low grade deposits. This resulted in the commercialisation (during the 1970s) of the NIMCIX technology, a continuous counter-current ion-exchange (CCIX) adsorption contactor that was developed by Mintek for the recovery of uranium from relatively low grade, un-clarified solutions. A number of pilot and commercial scale plants were built and operated successfully, including pilot plants at Rössing and Durban Deep, and full scale plants at Chemwes and Vaal River South. Currently, NIMCIX columns are still in use at Anglo Gold Ashanti's Vaal River South operation and Ezulwini, and they are being tested at Trekkopje on a relatively large pilot scale (referred to as Midi Commercial Demonstration plant with a heap stacking rate of a 9 000 t/day). The NIMCIX columns could be used for both adsorption and elution processes, but it has to be designed for the specific duty.

The use of resin-in-pulp (RIP) for the recovery of gold, uranium or base metals is still very limited in the Western World. One of the major uncertainties with regards to the commercial implementation of RIP has been the potential resin loss or consumption on a full scale operation. In recent times, all the major resin manufacturers have made significant technological advances resulting in a number of durable, commercially available, RIP-grade strong-base resins for the recovery of uranium. This has renewed interest in RIP as a potential economically attractive processing route for the recovery of valuable metals from low grade slurries.

Mintek has been conducting intensive research and development over the past 5 years on the recovery of uranium from low grade uranium slurries. The MetRIX™ technology, originally designed for the recovery of base metals from waste slurries, was evaluated for counter-current transport of resin and pulp. This technology is a joint development between Mintek and Bateman Engineering. The research included resin durability and metallurgical performance test work. Based on the results developed over this period, Harmony Gold Mining Company Limited commissioned Mintek and Bateman Engineering to demonstrate the MetRIX™ technology at their Harmony One Plant near Welkom in the Free State.

This paper summarises metallurgical results obtained during various laboratory studies, a pilot plant campaign on a uranium-bearing gold ore, and the demonstration plant operation.

2. EXPERIMENTAL

2.1 Laboratory Scale Test work

2.1.1 Equilibrium adsorption and elution isotherms

Eight point adsorption equilibrium isotherms were generated for the adsorption of uranium onto the strong-base anion exchange resin, in the sulphate form, by batch contacting the resin and uranium-rich pregnant leach solution (PLS) at different resin: solution ratios. Contact was made over a period of 24 hours under ambient conditions. After adsorption, the uranium-loaded resin was separated from the solution, washed to remove entrained solution, and then eluted in a column with excess eluate.

For the generation of elution equilibrium isotherms, a batch of resin in the sulphate form was pre-loaded from uranium PLS. The loaded resin was then contacted with eluant at 8 different resins: eluant ratios over a period of 24 hours. Upon completion of the equilibrium elution test work, the resin underwent an additional elution step using 2M HNO₃ to remove any residual uranium that might still have been present on the resin. The uranium stripped with HNO₃ was used to calculate the residual uranium concentrations on the resin.

2.1.2 Kinetics of adsorption and elution

The rate of uranium adsorption onto the ion exchange resin was investigated by contacting resin with a batch of uranium PLS, under agitation over a period of 24 hours. Regular sampling of the barren solution was done. The resin loading was determined by stripping the resin with excess 2 M HNO₃.

Uranium loaded resin was contacted with 110 g/L H₂SO₄ in batch under agitation. Regular samples were taken and analysed for uranium. At completion of the test, the resin was separated from the eluate and stripped further with 2M HNO₃ to determine the residual uranium concentration on the resin.

2.1.3 Pilot plant

The RIP pilot plant campaign for the recovery of uranium was run at Mintek during a three week period. During this time, the main focus was metallurgical performance of the resin and not durability. The pilot plant comprised of a leaching section in which uranium-rich ore was slurried with municipal water, and then leached under optimised conditions as determined during laboratory scale test work. The ore type used for the pilot plant was a siliceous gold ore with a U₃O₈ content of 150 – 350 g/ton.

The leach section was run in a sequential manner to ensure that there was a constant supply of freshly-leached pulp to the RIP adsorption circuit. This approach was taken to ensure that the leached pulp did not age, which might have caused speciation changes in the PLS over time (e.g. silica).

3. RESULTS AND DISCUSSION

Extensive laboratory investigations have been conducted at Mintek to evaluate the metallurgical performance of various strong-base anion exchange resins for the recovery of uranium. Various RIP-grade resins, which included both gel and macro porous types, were tested. These results, and those on new resins, are compiled into a data base which enables Mintek to recommend resins for specific applications in terms of metallurgical performance and resin durability.

The ion exchange resins are submitted to a series of basic batch tests, including the following:

- . equilibrium adsorption isotherm in the specific leach liquor/pulp,
- . equilibrium stripping isotherm, using different eluants,
- . rate of adsorption,
- . rate of elution and
- . laboratory and pilot-scale durability tests.

The test work described in this paper was done on a RIP-grade strong-base, macro-porous anion exchange resin. This resin was also used for the demonstration plant campaign. Only the metallurgical performance of the resin is discussed.

3.1 Laboratory test work results

3.1.1 Uranium adsorption equilibrium isotherms and rate of adsorption

3.1.1.1 Equilibrium and kinetics for Harmony leached pulp

Uranium equilibrium adsorption isotherm and kinetics of uranium uptake, obtained for Harmony-leached ore, are presented in Figure 1 and Figure 2. The Langmuir equilibrium isotherm provided the best fit for the equilibrium adsorption data with the determined constants as follows:

$$a = 55.929$$

$$b = 0.032$$

A McCabe-Thiele construction was done using the equilibrium isotherm generated. Resin to pulp ratio on the pilot plant was chosen to achieve 43 g/L U_3O_8 loading on the resin from a leached pulp containing 180 mg/L U_3O_8 with a target of <2 mg/L of U_3O_8 in the barren pulp after RIP.

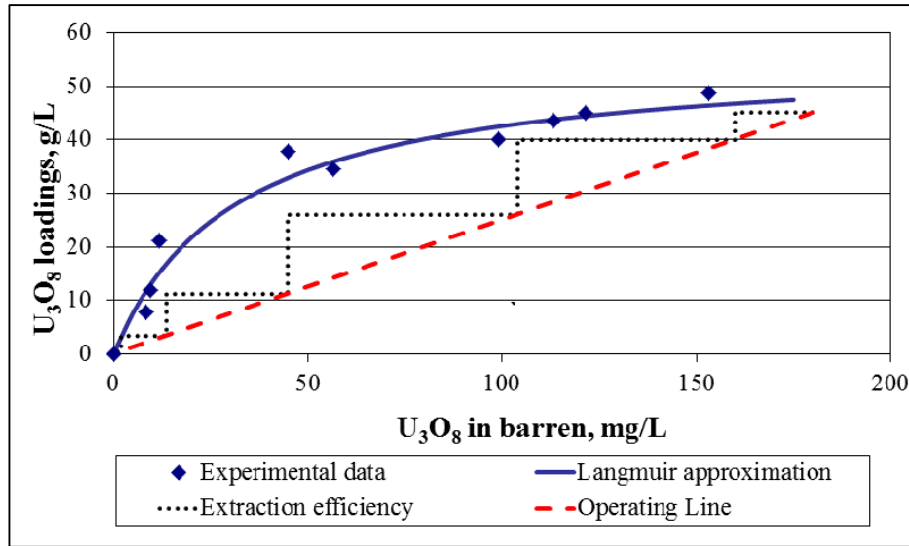


Figure 1: Uranium adsorption equilibrium isotherm (Harmony pulp)

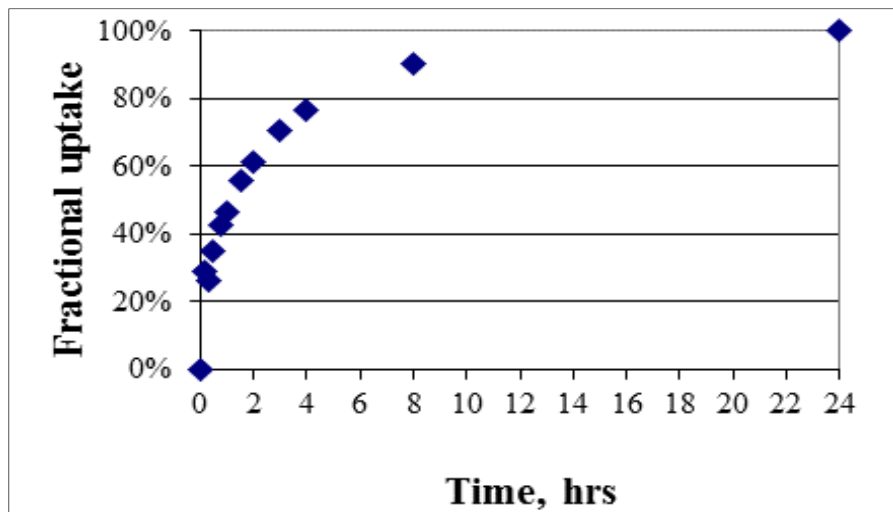


Figure 2: Rate of uranium adsorption (Harmony pulp)

3.1.1.2 Factors affecting uranium loading

Based on previous experience and information achieved during evaluation of RIP technology for uranium recovery from the Harmony ore type, the following factors were expected to have considerable impact on the resin performance:

- silica and
- chlorides

Silica present in uranium leach liquors is known to have an adverse impact on the rate of adsorption of the metal, especially when the silica levels on the resin become significant. Evaluation of silica impact on maximum uranium loading and rate of its uptake was reported previously in some of the published Mintek papers [1, 3]. For resin used in the current work, it was expected that the uranium adsorption capacity over a 24 hour period would decrease by >35% at silica fouling levels >20% (m/m).

Due to the negative impact of silica on the equilibrium and kinetics of adsorption, it was therefore targeted to limit silica fouling (e.g. limiting overall resin residence time in the adsorption circuit).

Another factor found to dramatically impact resin performance, was chlorides [6]. The source of chlorides in the current project was process water and the levels expected to be dealt with were 0 to 3 g/L. For prediction of the resin performance depending on the process water quality that might vary on a site, depending as well on the season, uranium adsorption equilibrium isotherms were generated using synthetic solution with different chloride contents. The isotherms were fitted with the Freundlich model and the constants are shown in

Table 1. The results obtained from the test work are given in Figure 3.

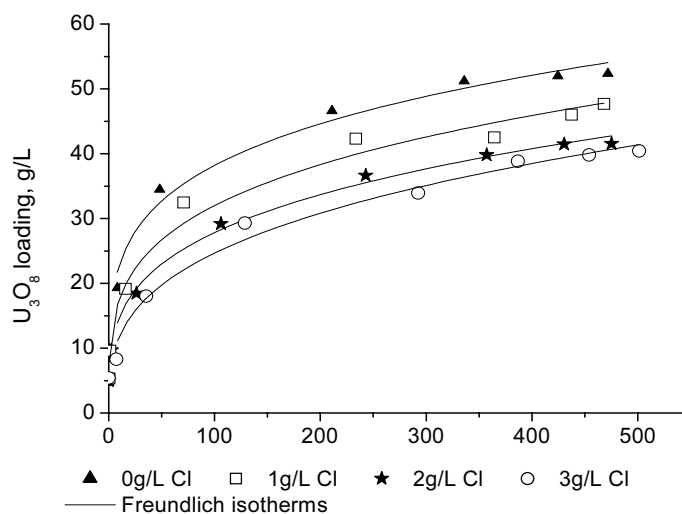


Figure 3: Uranium equilibrium loading: effect of Cl

Table 1: Freundlich equilibrium constants for uranium loading isotherms

Chloride concentrations in synthetic liquor	0 g/L	1 g/L	2 g/L	3 g/L
a	13.62	9.65	7.82	5.62
b	0.22	0.26	0.28	0.32

Quite a significant drop in uranium maximum loading was observed with an increase in the chloride concentration. The uranium loading was depressed by as much as 23% when the chloride content was increased from 0 – 3 g/L.

3.1.2 Elution equilibrium isotherm and rate of elution

Results of stripping equilibrium and rate of elution tests are presented in Figure 4. Equilibrium elution isotherms and rate of stripping indicated that uranium elution by using 110 g/L H₂SO₄ has an equilibrium constraint. For effective uranium stripping a specific volume of eluant was required. Results indicated that the rate of stripping would be less of a determining factor on the elution efficiency (with relatively long stripping resin residence times) achieving almost complete uranium elution after 3 hours.

The assumptions made based on equilibrium and kinetics of elution were confirmed by column elution tests, when stripping was performed at different flow rates (0.5 BV/h to 4 BV/h) as shown in Figure 5. There was minimal difference between the elution profiles observed within the flow rates evaluated, with almost all flow rates achieving 100% uranium elution after 17 BVs (bed volumes) of eluant were passed through the resin bed.

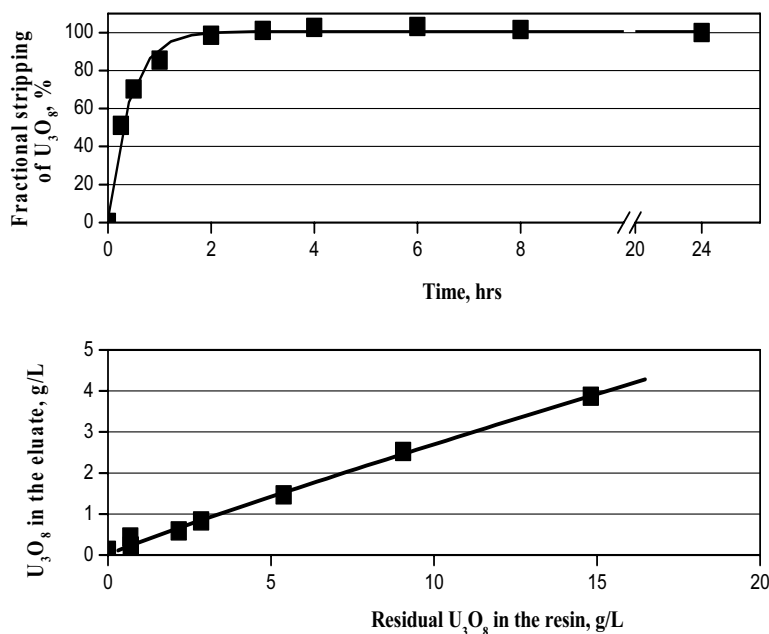


Figure 4: Equilibrium stripping isotherm and kinetics of uranium stripping with 110 g/L H₂SO₄ as the eluant

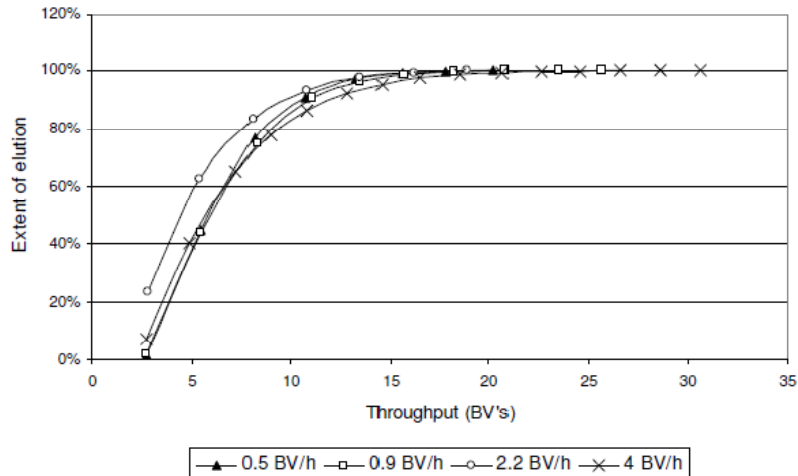


Figure 5: Effect of different flow rates on elution [2]

3.2 Pilot plant performance

Results obtained from the laboratory scale test were used to predict operating conditions for a pilot plant campaign using a relatively low grade uranium feed. The pilot plant was done essentially to confirm and optimise the operating parameters, including:

- number of adsorption stages,
- resin residence time,
- pulp residence time,
- resin loading and
- rate of silica fouling of the resin

The RIP section of the plant consisted of six 5 L, agitated RIP reactors. The reactors were set-up in series, in a manner that enabled the flow of pulp by gravity through the six reactors. Figure 6 shows a schematic diagram of the RIP section of the plant operation. The plant was operated in a carousel mode with continuous flow of uranium-leached pulp and counter-current batch movement of resin.

The fully loaded resin which exited the RIP adsorption stage from Position 1 went through an elution step before its re-entry back into the adsorption stage at Position 6.

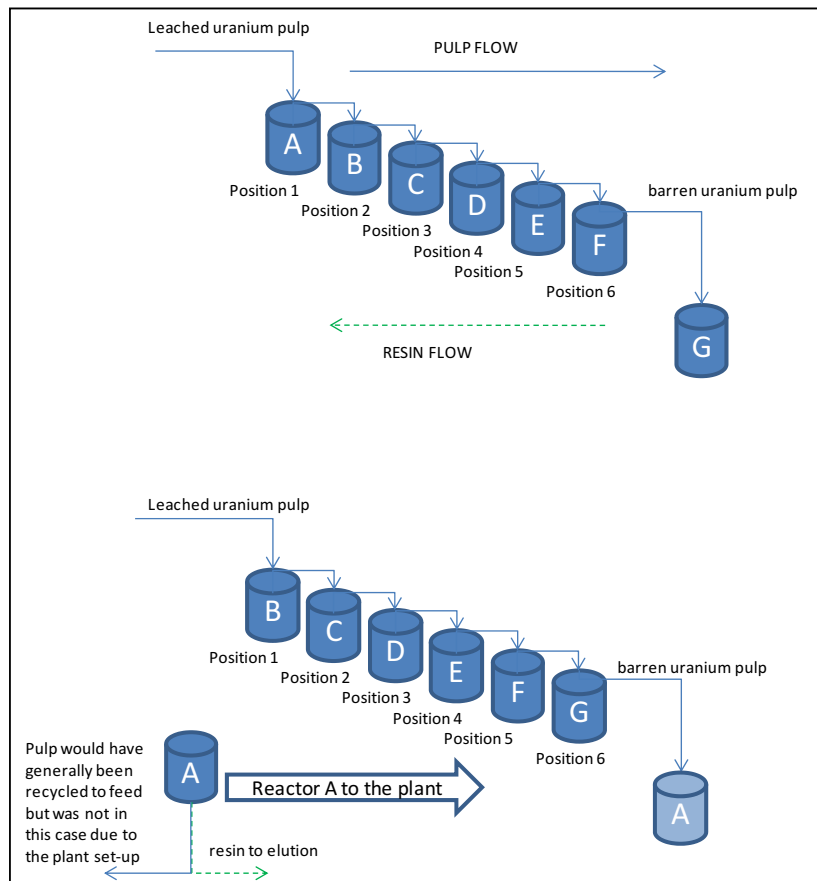


Figure 6: Flow diagram of the RIP pilot plant

Table 2: RIP pilot plant test conditions

Condition tested	1	2	3	4	5	6	7	8	9
Resin inventory per stage	1%	1.2%	1.2%	1.2%	1.2%	1.2%	1.2%	1.2%	1.6%
Resin residence time, hrs	2	2	2	2	2	2	2	3	3
Pulp residence time, min	30	30	24	24	30	37.5	37.5	37.5	37.5
Transfer numbers	1-16	17-26	27-36	37-43	44-51	52-72	73-80	81-93	94-100

The primary objectives of the RIP pilot plant was to investigate the impact of resin and pulp residence times on the efficiency of uranium adsorption, and the rate of silica build up on the resin. The conditions tested are shown in Table 2. The resin: pulp ratio was chosen based on the equilibrium isotherm presented in Figure 1. The chloride concentration in the pilot plant PLS was 0 g/L.

Uranium loading on the resin removed from Stage 1 varied significantly (Figure 7), primarily due to a variation in the uranium grades of the ore that was fed to the leach section of the plant. Uranium loadings of 30 – 48 g/L U_3O_8 were experienced for the most part of the campaign. These loadings were achieved at equilibrium uranium concentrations ranging from 64 to 276 mg/L in solution.

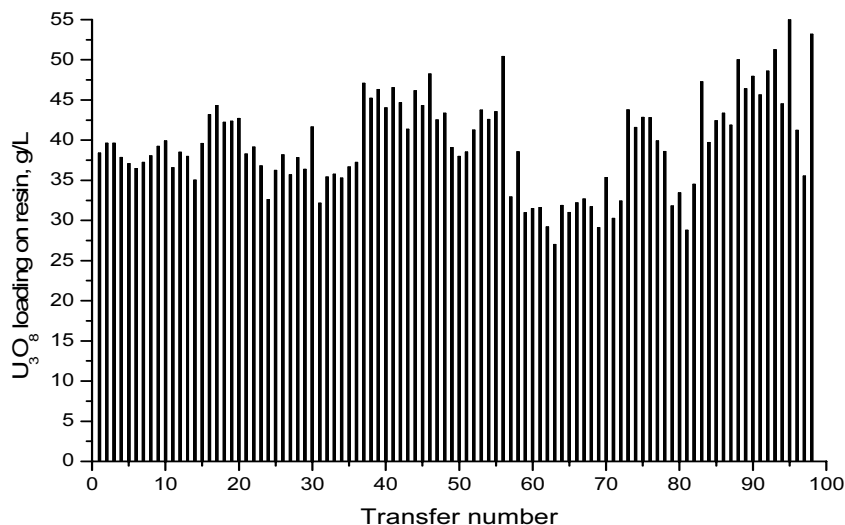


Figure 7: Uranium loading during the pilot plant campaign

The impact of resin residence time and pulp residence time on the maximum loading of uranium achieved was seen to be minimal within the parameters evaluated.

The uranium-loaded resin from Stage 1 was eluted with 110 g/L H_2SO_4 at a rate of 5 BV/hr until a total of 30 BVs was passed through the resin bed. These conditions were found to be optimal for consistent stripping of U_3O_8 from the resin to below 1g/L. Such residual uranium content on the eluted resin did not have an impact on the adsorption performance in RIP.

Build-up of silica content on the resin was closely monitored during the pilot plant in order to determine a rate of silica fouling. As silica loads on the resin a portion of it was eluted with acid together with uranium (“strippable” silica) and the other portion remained on the resin (“un-strippable”) silica. Remained silica could be stripped only with caustic and was allowed to build up for duration of the plant. Thus, rate of “un-strippable” silica was determined.

The SiO_2 content in the PLS over the duration of the pilot plant was <500 mg/L. Profiles of “strippable” and “un-strippable” silica observed during the pilot plant campaign are shown in Figure 8. The level of “strippable” silica was seen to be constantly below 5 g/L (1% m/m); while a constant build-up in “un-strippable” silica levels was observed. A steep gradient in “strippable” and “un-strippable” silica observed between 45 and 55 hrs of plant operation was as a result of an excessive acid addition in the leach circuit. This caused excessive silica to be brought forward to RIP circuit. As the campaign proceeded, it was clear the amount of ‘un-strippable’ silica increased progressively.

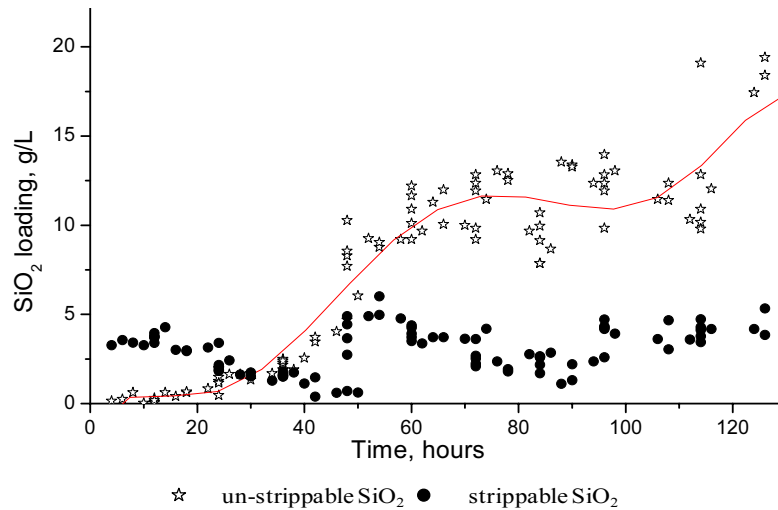


Figure 8: Silica fouling of the resin during the pilot plant campaign

3.3 MetRIX™ demonstration plant

Results obtained during the extensive laboratory and pilot test work conducted at Mintek were used for evaluation of the MetRIX™ technology as an option for recovery of uranium from Harmony's gold ore. Based on the potential capital and operating cost savings when compared to the other processing flow sheets considered [7], Harmony commissioned Mintek and Bateman to install and operate a MetRIX™ demonstration plant on their Harmony One Plant near Welkom in the Free State. A photograph of the plant is shown Figure 9. The demonstration plant was operated over a 47 day period.



Figure 9: Demonstration plant installed on site at Harmony

3.3.1 Process description

The demonstration plant incorporated 4 main sections namely, leaching, RIP adsorption, elution and finally, a neutralisation circuit to treat the barren pulp and effluents exiting the plant. The neutralised slurry was returned to Harmony's gold recovery circuit. A simplified flow diagram is given in Figure 10.

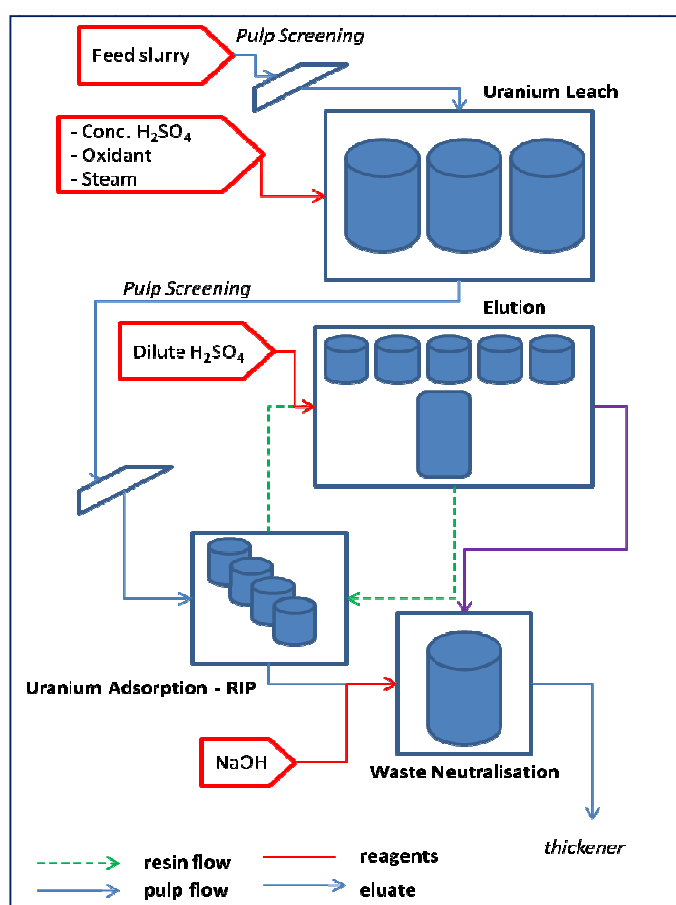


Figure 10: Simplified flow diagram of the METRIXTM demonstration plant

3.2 Uranium leaching

A bleed of Harmony's gold ore thickener underflow was used ('reverse' leach approach) as feed to the uranium leach circuit. Laboratory leach test work at Mintek provided leach parameters for the design of the leach circuit. However, a reduced residence time was employed to limit the costs of the leach circuit that would still provide relatively efficient uranium leaching. Concentrated sulphuric acid (98%) was used to target a pH 1.7 during leaching. MnO₂ was used to control the Eh to about 450 mV (Ag/AgCl). The leach temperature of 50°C was achieved via direct steam injection.

Three leach tanks were implemented to operate sequentially on a batch basis, thus ensuring a consistent supply of leached pulp to the RIP plant.

Uranium leach efficiencies of between 72% - 85% were achieved. This was comparable with laboratory scale leach test work for the leach residence time allowed.

3.3 RIP adsorption circuit

Pre-screening of the leached pulp was done in order to remove woodchips, plant debris and grit. It was decided to install only 4 adsorption stages to limit the overall costs of the plant. A different operating line to the one tested during the mini-pilot plant was used in order to achieve 100% uranium recovery over 4 stages. The adsorption stages were mechanically agitated.

A schematic layout of the RIP adsorption circuit is given in Figure 11. Submerged screens were used to separate the resin from the pulp in the tank. Pulp was transferred from stage to stage via gravity. Eductors were used for resin transfer from the bottom of the RIP tanks onto the sieve bends at the top of each RIP tank. The purpose of the sieve bends was to facilitate the movement of resin from tank to tank, whilst the pulp returned to the tank from which it was pumped. The pulp moved counter-currently to the resin, with fully loaded resin exiting from RIP 1 tank and eluted resin entering the adsorption circuit into the RIP 4 tank. Leached pulp entered the adsorption circuit at RIP 1 and exited from RIP 4.

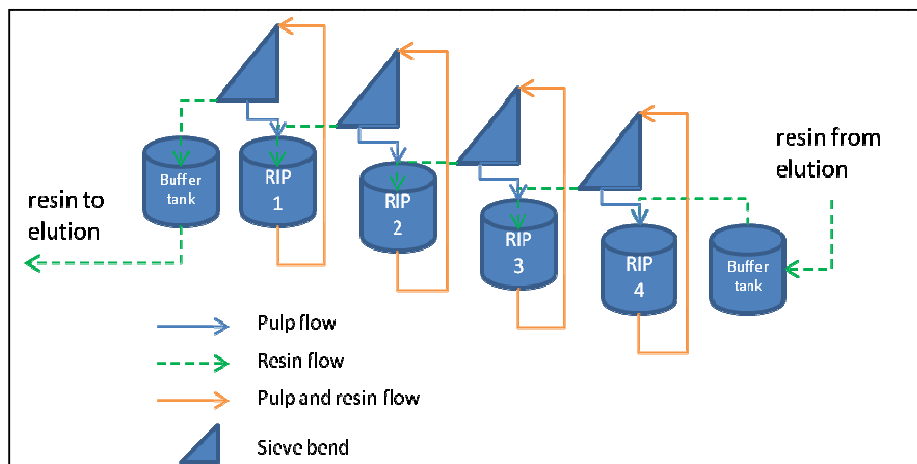


Figure 11: Simplified flow diagram of the RIP section of the plant

A McCabe-Thiele construction was done on the equilibrium adsorption isotherm produced from a synthetic solution containing 2 g/L Cl^- (at equilibrium with 470 mg/L U_3O_8 in solution), represented in Figure 3. The demonstration plant results were plotted on the isotherm (Figure 12). An assumption was made that 80% approach to equilibrium per stage would be achieved. A uranium loading in excess of 29 g/L U_3O_8 was achievable with a resin and pulp flow rate of 4.5L/h and 2.4m³/hr respectively. This data was achieved during a time when the plant was stable, with the uranium content of

the PLS at 80 mg/L U_3O_8 and a barren pulp containing <5 mg/L U_3O_8 in solution. Much higher uranium loadings were achieved during the pilot scale test work, however the PLS did not contain Cl^- and had significantly higher U_3O_8 concentrations in the PLS.

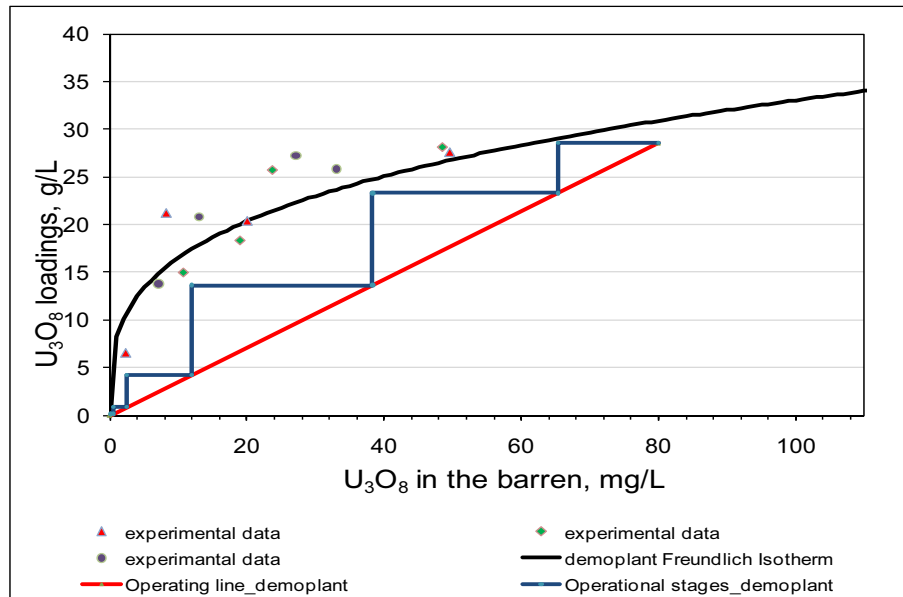


Figure 12: Demonstration plant adsorption equilibrium isotherms

The silica fouling rate on the demonstration plant was within the limits predicted based on the laboratory and pilot plant test work.

3.4 Elution circuit

The loaded resin that exited the RIP 1 tank was collected in a designated buffer tank and once a sufficient volume of resin had been accumulated, an elution cycle was done. Sulphuric acid at a concentration of 110g/L was used to strip the uranium loaded resin. The elution section consisted of the following tanks:

- fresh eluant containing 110 g/L H_2SO_4 ,
- 2 intermediate eluates,
- a strong eluate tank containing uranium-rich fraction and
- a wash water tank

The elution circuit was run in a closed loop, with only the uranium-rich fraction exiting the circuit after each elution cycle.

Uranium-rich eluate contained between 1.9 and 3.6 g/L of U_3O_8 . Such uranium concentrations were relatively low (when related to the stripping isotherm in Figure 4) due to the limited number of intermediate eluate tanks and ineffective manual control of

the relative resin and eluant volumes. About 30 BVs of eluant was passed through the resin column over a 6 hour period, consistently resulting in a residual uranium concentration of < 0.8 g/L on the resin.

4. CONCLUSIONS

Extensive laboratory and pilot scale test work at Mintek resulted in the selection of the most cost-effective operating conditions for the recovery of uranium from acidic-leached slurry via RIP. The pilot plant and demonstration plant adsorption and elution results correlated reasonably well with the predictions that were made from the laboratory test work. Moreover, these results confirmed the improved performance of the MetRIX™ technology under the optimised operating conditions employed.

The demonstration plant campaign was successful and achieved the following:

- The MetRIX™ RIP process was successfully demonstrated and the process targets were achieved.
- A relatively low rate of SiO₂ fouling was measured under the final optimum operating conditions.
- Sufficient elution data were generated for the elution strategy optimization that would be employed on the full scale plant.

Demonstration of MetRIX™ technology gave Harmony more confidence in implementation of RIP technology for uranium recovery from their gold ore. Commercialisation of MetRIX™ technology in South Africa would give a boost for RIP application in various hydrometallurgical areas (base metals, rare earths, etc.).

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I initially worked in the extraction group on laboratory and pilot scale investigations for base metal recovery. Thereafter moved to the processing group and worked on laboratory, pilot and demonstration plant test work (at Harmony Gold Mining Company Limited) for the recovery of uranium via RIP process routes.

