REMOVAL OF URANIUM FROM MINE WATER USING ION EXCHANGE AT DRIEFONTEIN MINE

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ABSTRACT

Mine waters from gold and sometimes coal mining contain low but potentially harmful levels of uranium. These are not easily removed by conventional treatment technologies such as lime precipitation.

The use of ion exchange resins for the recovery of uranium from water sources in especially mine water circuits is commonplace and can be considered to be state-of-the-art for medium to low uranium concentrations.

A pilot plant was operated at Driefontein mine to determine the ability of ion exchangers (Lewatit Monoplus S6368) to reduce low levels of uranium to below acceptable International Discharge Limits. Results show that uranium can be reduced to below 10 µg/ℓ consistently, and that the uranium can be effectively eluted from the ion exchange resin. The selected resin showed a very high affinity for uranium, resulting in very long run times and hence giving extremely low operating costs.

Data has been obtained for engineering design purposes, and has exposed the particular challenges of long cycles and high flowrates. The process is both technically and economically feasible, and a full scale plant is under consideration.

1. INTRODUCTION

Ion exchange resin has been used for many years in the recovery of uranium from both primary uranium producers, and from gold and copper mines as a byproduct.

The current gold reefs mined at Gold Fields' Driefontein mine contain low levels of uranium. Small amounts of this uranium dissolve during normal operation of the mines. This water is being used for cooling of the mines underground recycled back to the fridge plant. Saturated air escapes from the circuit on surface. A small amount of the process water is used in the gold plant and finally discharged onto the tailings storage facility as sludge, where uranium is leached and transported into the water system causing a uranium build-up. The water will enter the dewatered zone above the mining activities and return to the process water circuit. A simplified circuit of the mine process water is shown in figure 1.

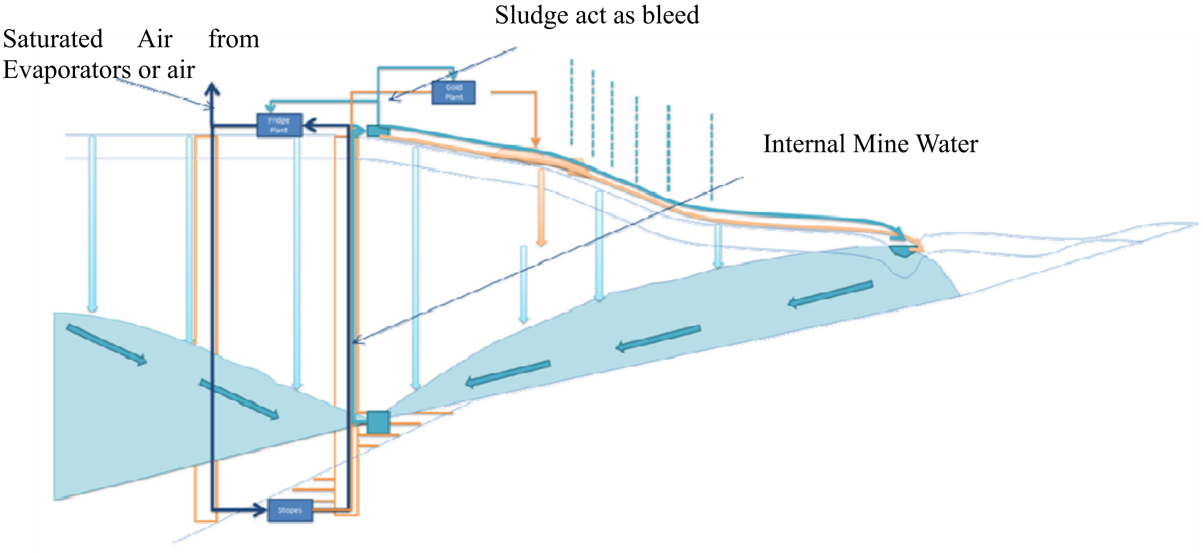


Figure 1. Mine Process Water Circuit.

Water Standards (DWAF, 1996) and (WHO, 2008)

Uranium is one of the nuclides that contribute to the radioactivity in water. Traces of uranium are found in all soils as well as fresh water (0.4 µg/ℓ) and sea water (3.2 µg/ℓ). Substantially higher concentrations of uranium are found in association with mineral deposits of uraniferous minerals. In general the effects of exposure to elevated levels of radioactivity in water are an increase in cancer risk. Uranium tends to accumulate in the kidneys and the liver, where, chemical toxicity is of more concern than the risk of cancer. The target water quality as suggested in by the Department of Water Affairs and Forestry is between 0 and 70 µg/ℓ Uranium. The provisional guideline value for uranium in drinking-water as specified by the World Health Organization is 15 µg/ℓ based on its chemical toxicity for the kidney. The contribution of drinking-water to total radiological exposure (potential cancer risk) is typically very small.

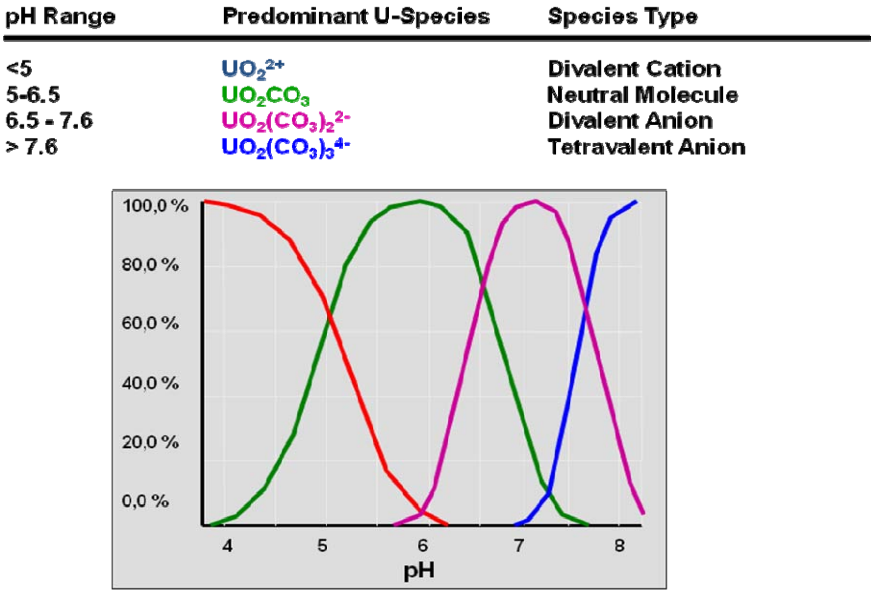
Partnership Gold Fields, Lanxess and Cwenga Technologies

Cwenga Technologies has been the Southern African representatives for Lanxess ion exchange resins since 2001. The two companies have been involved in development of various environmental projects involving ion exchange in the mining industry. Since 2006 there has been a project in place between Gold Fields and Lanxess in the development of a process for the removal of uranium at very low concentration in mine water.

2. BACKGROUND

Water Chemistry

The mine water at Driefontein Gold Mine ranges between pH of 7.7 and 8.4. Under the pH conditions of the feed water, it can be seen from figure 2 that the primary uranium species will be the anionic form: $UO_2(CO_3)_3^{4-}$. The anionic uranium complexes are soluble in water over wide pH ranges.



pH Range	Predominant U-Species	Species Type
<5	UO_2^{2+}	Divalent Cation
5-6.5	UO_2CO_3	Neutral Molecule
6.5 - 7.6	$UO_2(CO_3)_2^{2-}$	Divalent Anion
> 7.6	$UO_2(CO_3)_3^{4-}$	Tetravalent Anion

Figure 2. Relationship between pH and uranium ion.

Resin Chemistry

Lewatit MonoPlus S6368 is a strongly basic, gelular anion exchange resin with beads of uniform size. The resin has a lifetime of at least 2 years and is able to operate at temperatures ranging from 0 to 70 ºC and at a pH of up to 12.

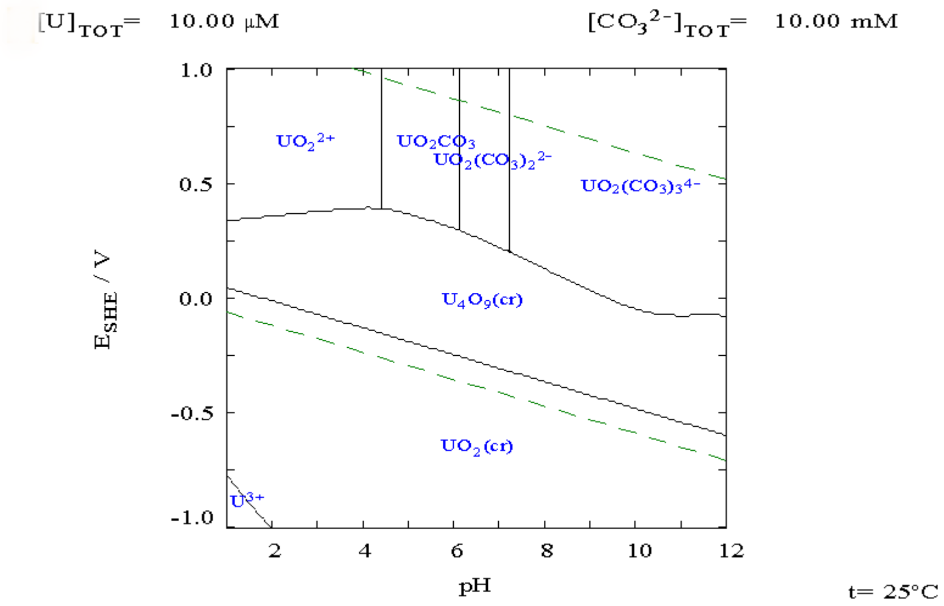


Figure 3. Uranium Chemistry

The higher the ion change of the molecule, the more selective the resin will be towards the species (see figure 4). Therefore the uranyl carbonate complex has a very high selectivity for the ion exchange resin, Lewatit MonoPlus S6368. This means that exhaustion of the resin will take a long time, but at the same time it will also be possible to remove uranium to very low levels. The regeneration of the resin requires a very large excess of chemicals due to the high selectivity of the resin. During loading the uranium complex will absorb onto the active site of the resin and displace the sulphate ion (figure 5.a). The uranium complex is eluted during regeneration with sulphuric acid. The sulphate ion will adsorb onto the resin, while producing a uranyl sulphate complex and carbon dioxide (figure 5.b).

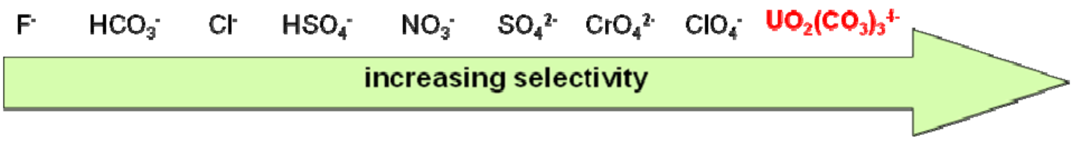


Figure 4. Resin selectivity.

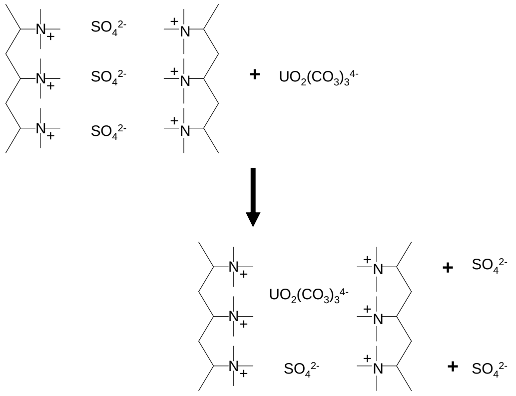


Figure 5.a. Resin Loading Chemistry

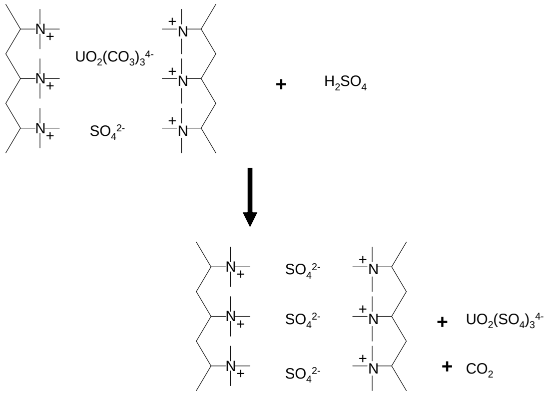


Figure 5.b. Resin Regeneration Chemistry

The maximum theoretical loading of Lewatit MonoPlus S6368 is shown in table 2.

Table 2. Resin Capacity.

total molar capacity of SBA resin:	1,1 eq/L
molecular weight Uranium:	238 g/eq
exhausted equivalents per mol Uranium:	4
total gravimetric capacity:	65 g/L

The strong base anion resins have been used in South Africa at Vaal River Operations for the last two decades. More recently First Uranium has installed a resin plant for the recovery of uranium. In Namibia, Rössing Uranium and Langer Heinrich are using resin for recovery of uranium and there is a new mine under development by Uramin at Trekkopje. There is a plant in Malawi that will come on line in 2009.

Outside of Africa there are applications at:

- Key Lake in Canada,
- Olympic Dam, Australia,
- Smith Range, USA,
- Crow Butte, USA, and
- Navoi, Uzbekistan
- and various mines at Kazatomprom.

There have been a number of contaminated ground waters near Berlin that have used ion exchange resin for removal of uranium from water for environmental reasons. One example is as follows:

Test Results of a Campaign in South-Germany (GUTEC / Krueger WABAG/ Bavarian Regional Government) (Neuman & Fries, 2009)

Feed Composition		
Uranium	12	µg/L
Nitrate	16	mg/L
Sulfate	65	mg/L
pH	6.5	
Resin used		
LEWATIT® S 6368, sulfate form		

Performance		
Uranium out:	0.07	µg/L
Removal rate:	> 99%	
Treated Bed Volumes:	40 080	
Uptake:	4.8 g/L	
Breakthrough:	not yet occurred	

Chemistry of Mine Water

Driefontein's mine water quality is shown in table 3.

Table 3. Mine water quality.

Element	Concentration (mg/ℓ)	Element	Concentration (mg/ℓ)
Suspended solids	12	pH	7.5
Oil & grease	6	Conductivity	2300
COD	10	Uranium	0.234
Chloride	150	Nickel	0.251
Sulphate	1140	Cobalt	0.174
Calcium	210	Copper	0.012
Magnesium	53	Iron	0.144
Sodium	190	Strontium	1.200
Nitrate	49	Thorium	0.0034
Manganese	0.160	Fluoride	0.59

3. TEST WORK PROGRAMME AND EQUIPMENT

The pilot plant shown in figure 6 was constructed to test the efficiency of the ion exchange technology on the mine process water. The pilot plant was designed with a process capacity of 2 m^3/h and has been in operation 24 hours a day for a period of 6 months. Samples were taken daily for metal analysis. The plant consists of two sections: pre-treatment and uranium ion exchange.

Figure 6. Mine Process Water Pilot Plant

The pre-treatment (figure 7) involves dissolved air flotation (DAF) for the removal of oil and grease, also to achieve a partial solids removal. This is followed by a disinfection step using sodium hypochlorite for the control of micro biological growth in the water. The water then passes through a coagulating sand filter for the removal of suspended solids and colloidal uranium, followed by granular activated carbon filtration (GAC). The GAC removes dissolved organic compounds (DOC), residual oils and greases, and de-chlorinates the water. The pre-treatment section protects the ion exchange section from suspended solids, organics and oil and grease, which can poison the resin and decrease the efficiency of the uranium removal.

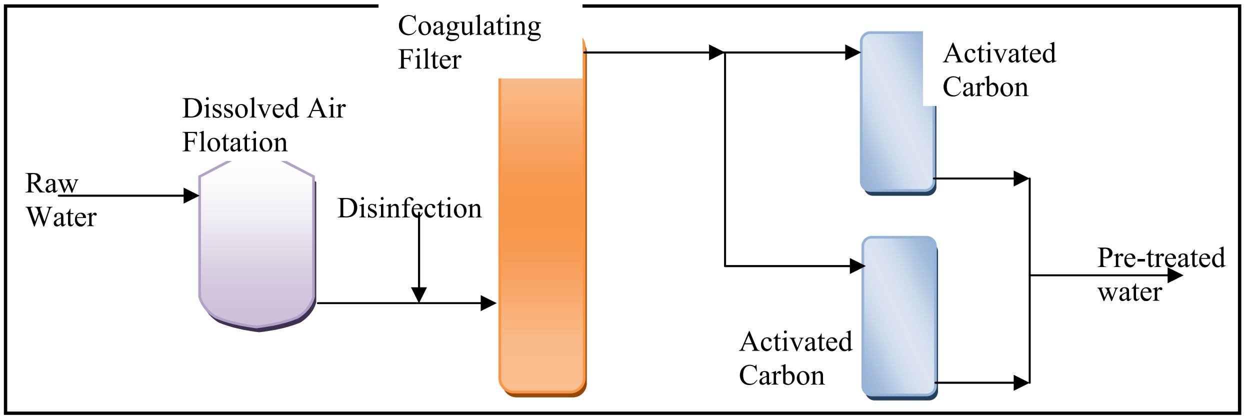


Figure 7. Pre-treatment Section

The water then proceeds to the uranium ion exchange section. The ion exchange configuration is shown in figure 8. There are two lead columns, one in operation and one on standby/regeneration. The aim is to reduce the uranium concentration below 20 µg/ℓ. The lead columns contain 100 ℓ of Lewatit MonoPlus S6368 resin and operate at 20 bedvolumes per hour. This is followed by a polishing (or lag) column using the same resin, ensuring that the target uranium concentration of 10 µg/ℓ is achieved. The columns are operated as packed beds in an up-flow direction with countercurrent regeneration. During regeneration 15 % sulphuric acid is pumped through the lead column at a rate of 0.25 bedvolumes per hour for 4 bedvolumes and then rinsed at a rate of 0.25 bedvolumes per hour for 4 bedvolumes. Regeneration only applies to the lead columns.

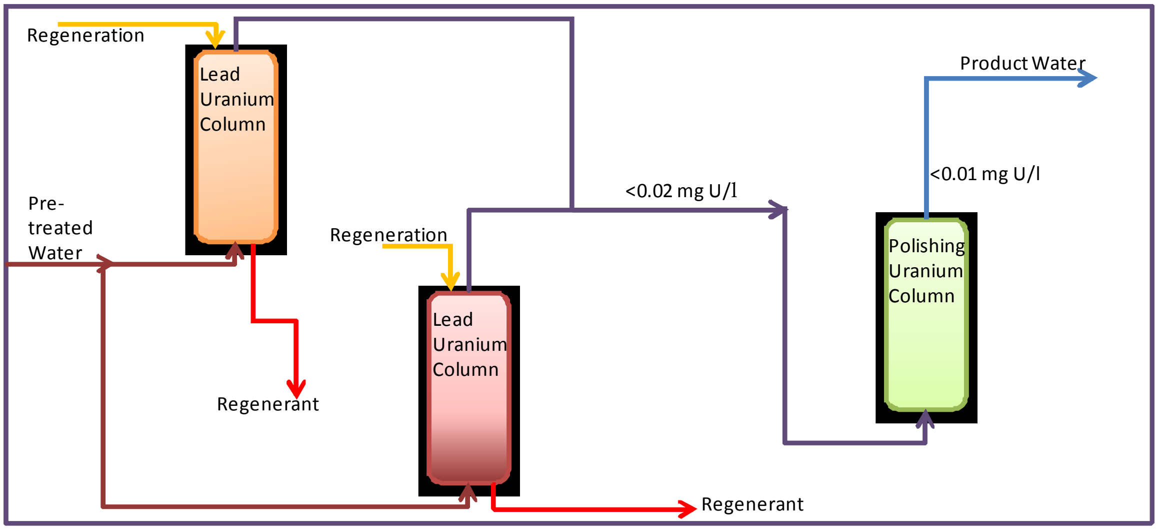


Figure 8. Ion Exchange Configuration.

4. RESULTS

The graph indicates that the operating capacity of the resin will be less than the maximum thoeretical loading due to the presence of sulphates in the mine water and the feed concentration of uranium. The operating capacity obtained at Driefontein was 4.5 g/l which appears to be inline with the theoretical figures.

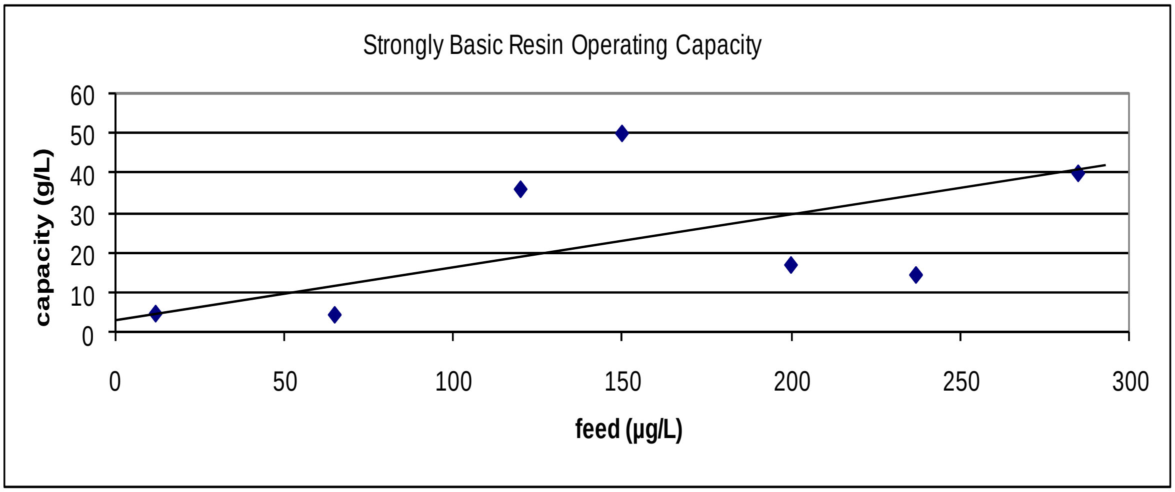


Figure 9. Resin Operating Capacity. (Neuman & Fries, 2009)

The exhaution time for the resin under trial conditions was three months (figure 10) in the initial testwork. The presence of suspended solids caused the resin to be clogged after 6 weeks operation and the bed was backwashed. This disturbance of the bed reluted in higher leakeages which can be seen from the graph.

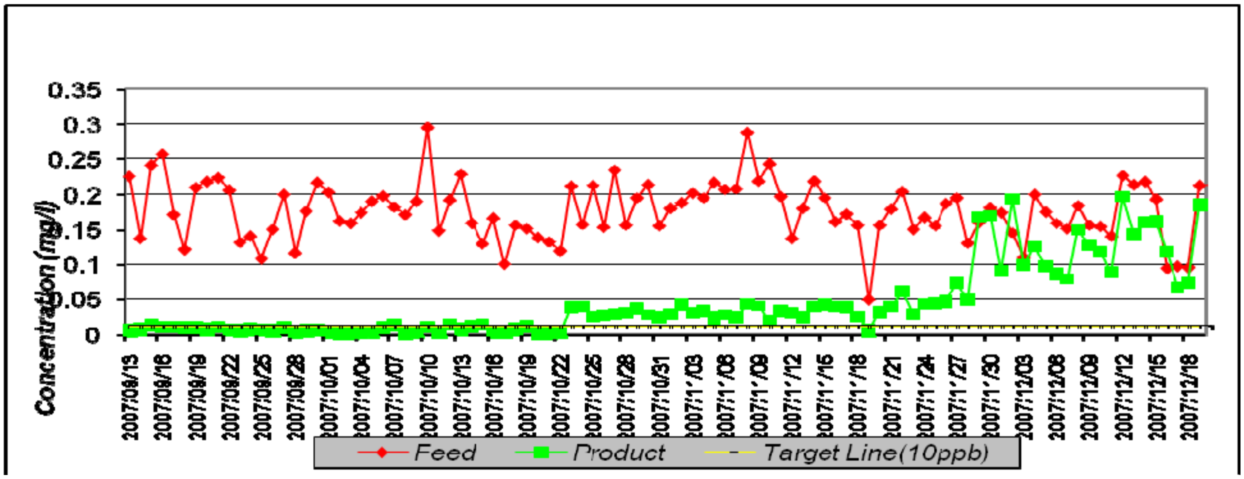


Figure 10. Loading Performance.

The performance of the uranium removal section in the pilot plant is shown in figure 11. The water was fed to the uranium columns at a rate of 20 bedvolumes per hour. The uranium removed in the coagulating filter was only a very small amount. The bulk of the uranium present in the plant was removed in the lead uranium columns. All the slippages in the plant was successfully covered by the lag uranium removal column. Breakthrough of the resin was still not achieved after treating 5400 bedvolumes of mine water.

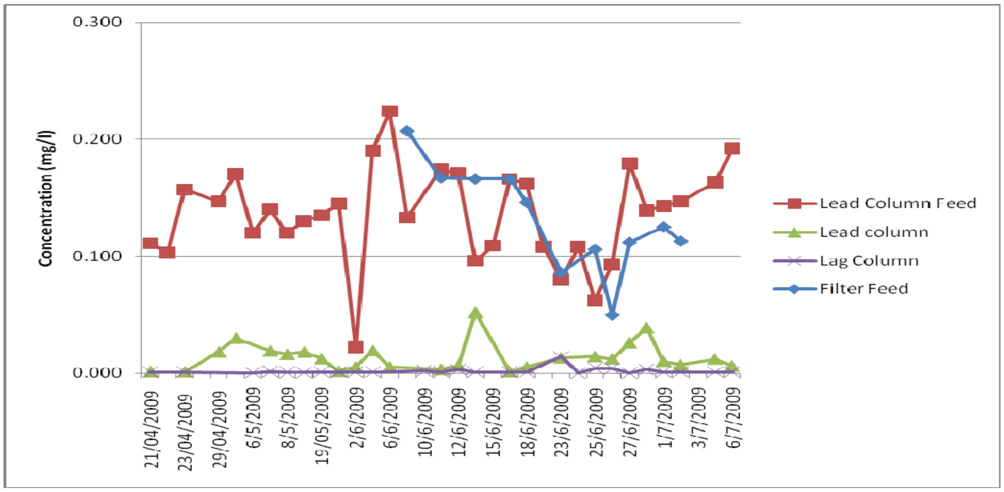


Figure 11. Pilot plant performance.

Due to storae of feed there is some delay in concentration from feed to the lead inlet, indicated by the feed being lower than the lead column.

Elution of Resin

The 15 % sulphuric acid solution used in the regeneration of the resin was successful in stripping the uranium from the resin. Low flowrates during the regeneration of the resin meant that it was difficult to control on the pilot plant. This had the effect that the elution curve is flatter than what would otherwise be expected. The start of the rinse cycle is indicated by the arrow in figure 10. A higher flowrate during rinsing will elevate the situation and it is our intention to do so in further regeneration. The water recovery on this plant was over 99.9%.

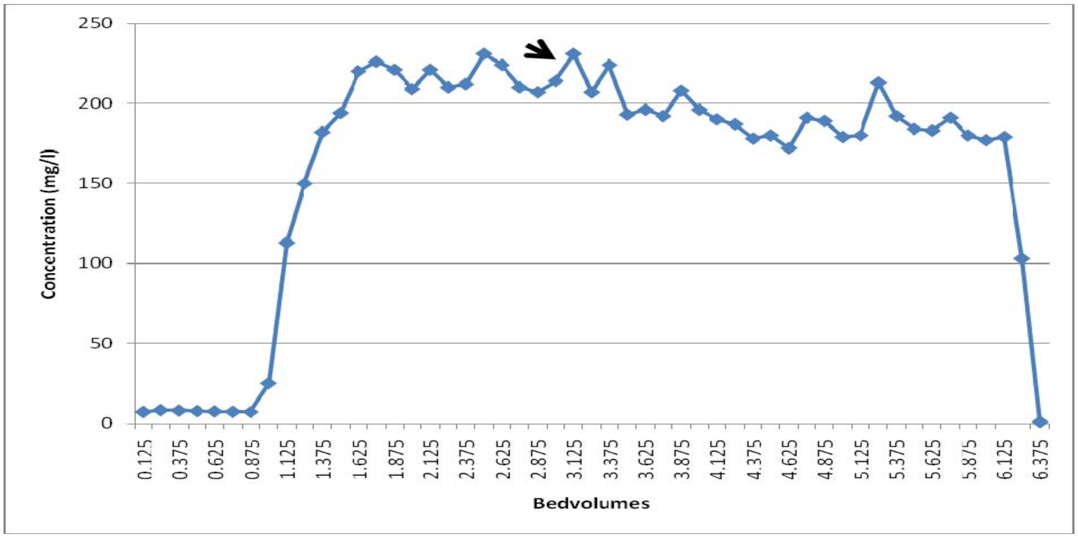


Figure 10. Elution curve

5. ECONOMICS OF RESIN USE

Capital costs of pre-treatment are quite high when dealing with process water as there are variable and unknown potential contaminants. The capital costs for the uranium removal plant with an operating capacity of 7.5 Mℓ/day are shown in table 4.

Table 4. Capital Costs

Description	Cost
Coagulating Sand Filtration	R 17 031 000
Granular Activated Carbon	R 9 468 000
Uranium Ion Exchange	R 14 803 000
Pumping	R 5 202 000
Storage	R 2 288 000
Total	R 48 792 000

Operating costs are in the order of R 0.2 per kℓ.

Resin Costs = R 0.15 per kℓ
Power and Chemicals = R 0.05 per kℓ
Labour and Maintenance = R0.01per kℓ

By being in a partnership with a uranium and gold mine it is possible to reuse the resin in the polishing column and thereby minimize replacement costs. The spent regenerant can be taken off to the uranium plant, as can uranium contained in suspended solids. This will result in a payment for the uranium recovered. The spent carbon can also be taken off to gold CIP circuits.

If payment can be obtained for the uranium, this will cover the cost of the ion exchange resin, at present uranium and resin costs. This would be an internal accounting issue.

6. CONCLUSION

It was clear from the pilot plant work that pre-treatment is critical to successful implementation of uranium removal. In particular it was noted that colloidal uranium is removed by filtration. Bacterial growth was observed and needs to be controlled as the cycle times are very long. There was also some degree of organic fouling on the ion exchange resin also a result of long cycle times. Even low levels of solids in suspension resulted in blockage of the columns.

The uranium columns had a limited loading capacity due to water chemistry and it was noted that it is critical to limit bed mixing especially in the polishing column. Regeneration of the lead column requires low regenerant flow rates and long contact times.

The long cycle time require careful consideration to pressure drop and bed compaction. The polishing column is required to ensure compliance with WHO standards.

Radioactivity is not a danger from the point of view of loaded resin and no jacketing of the vessels is required. However in loaded uranium resin has to be disposed of according to national legal requirements, based on experience elsewhere.

Lewatit 6368 was successful in removing uranium from the mine water circuit down to levels of 10 µg/ℓ, below to the World Health Organization standards. The regeneration of the resin proved to work, but the rinsing strategy needs to be improved. The lead-lag configuration of the uranium removal section showed improved water quality compared to a single column.

Costs involved in the uranium removal from mine water are relatively low.

7. REFERENCES

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