

# Improved dewatering characteristics of uranium tailings through controlled neutralisation for paste disposal

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## Abstract

*Tailings from a uranium mine have been tested to improve dewatering properties and final wt% solids of the neutralised tailings. The objectives were to maximise water recovery due to the scarcity of water in the project area and to produce a suitable cemented paste fill to minimise ore dilutions underground in order to maximise the head grade to the mill. Applicability of the controlled neutralisation process where gypsum would precipitate as crystalline particles improving dewatering properties of the tailings via deep bed paste thickeners was tested. Acid leach slurry samples used were from the end of resin-in-pulp (RIP) process after uranium recovery but before neutralisation of the slurry. The tests conducted indicated that the controlled neutralisation process greatly reduced the volume of neutralisation precipitates which typically results in a higher final density and wt% solids. Additionally it showed improved dewatering (filtration) properties. Controlled neutralisation also reduced the amount of sulphate in the solution close to that of its saturation limit, which would reduce the amount of scaling that could occur during full scale applications and would increase the recyclability of the water back to the process. Deep bed paste thickener also improved the final wt% solids of the underflow. The test work demonstrated that it was possible at the bench scale level to improve final density and recover additional water. From the final density observed as part of the current test work, without any scale up, 10 to 15% of extra water could be recovered. The increase in the filterability of the material provided a good indication that further increases in wt% solids could be obtained. Unconfined compressive strength (UCS) tests showed improvements for samples with reduced gypsum concentrations. Although further studies are required, neutralisation of uranium tailings under controlled conditions to reduce gypsum content and form gypsum as crystalline particles could provide a viable option in the preparation of suitable paste backfill materials.*

## 1 Introduction

For a new developing uranium milling and processing facility, uranium ores are planned to be leached with sulphuric acid. The resulting uranium leach residues (i.e. tailings) contain high acidity with extremely low pH (e.g. pH <1). They had to be disposed of to a tailings pond. The original feasibility studies prepared to obtain permits for the development of the mine considered about 49 wt% solids for tailings. The pilot studies conducted on the ore samples taken from the mine to assess and develop an uranium recovery process indicated the generation of tailings with very low wt% solids content (e.g. <30%). The recovery of water in larger quantities and reduction of footprint for disposal of tailings were requested by the authorities to obtain permits to develop and operate. Uranium leach residues (i.e. tailings) received from sulphuric acid leaching process typically have poor dewatering properties resulting in production of tailings with low wt% solids content and relatively large volumes. These tailings would require a large area for disposal and storage and would cause large water losses. The main interest was to maximise water recovery due to the scarcity of water in the area and to minimise ore dilutions underground by the use of cemented paste fill in order to maximise the head grade to the mill. Thickened tailings and paste options were investigated for the purpose of surface disposal.

Leach residues require neutralisation before their disposal due to their high acid content. The most common neutralisation process currently practiced by the industry involves addition of lime to the waste material to

increase the pH to a certain level. This application usually takes place in one step (i.e. straight lime neutralisation process), which typically generates ultra fine, low solids density gypsum and metal hydroxides by-products. The gypsum quality is undesirable as it is voluminous and has a high surface area.

Also, equipment scaling in tanks, pipelines and mixers is generally more troublesome. It is believed that this low density gypsum and metal hydroxides formation was one of the main reasons for not achieving higher wt% solids during the settling and dewatering assessment previously carried out by Golder PasteTec on as received neutralised tailings.

Testing on tailings straight neutralised to a pH of 10 demonstrated that thickened tailings slurry at around 40 wt% solids could be achievable using a high compression thickener. The wt% solids could possibly be increased further by the use of a deep bed paste thickener. Due to the fine particle size and gelatinous nature of the tailings it was not expected that the wt% solids could be increased significantly. For instance, it was questionable to obtain wt% solids of 49 which would be needed to obtain a thickened tailings/paste with a measurable slump (< 250 mm).

In acid mine water treatment projects, it was found that controlled neutralisation where gypsum could precipitate in crystalline form could generate denser wt% solids, smaller volumes and precipitated material which could easily be filtered to obtain higher wt% solids (e.g. 60%). These processes are called high density sludge (HDS) lime neutralisation/precipitation method and found to be especially feasible for treating high strength acid mine waters (Kuyucak et al., 1991; Kuyucak et al., 2005). The similar process principles were intended to be adapted to the neutralisation of the leach solution and leach slurry. The objective of this study was to assess the effect of gypsum crystal growth by the controlled neutralisation process. As an alteration to the controlled neutralisation process, sequential neutralisation where gypsum could separately be formed and removed from the medium was also tested.

## 2 Material characterisation and methods used in characterisation

Slurry samples received for testing was the material from the pilot scale lab tests conducted for assessment and development of the uranium recovery process. The sample tested was the leach slurry resulting from the acid leach test work performed on uranium ore. Typically the sample tested would have been the leach slurry after it had undergone uranium recovery by the RIP process but before slurry neutralisation.

All samples received by the Golder PasteTec Material Characterisation and Process Development Lab were subjected to material property characterisation tests to establish physical and chemical properties of sample prior to neutralisation. The tests conducted, methods used and results obtained are given below.

### 2.1 Particle size distribution (PSD)

The particle size distribution was determined using mechanical sieving and/or Fritsch laser particle size analyser according to ASTM D4464-00 (2005). For the particles larger than 150  $\mu\text{m}$  were sieved prior to laser analysis. Specific D-values are represented in Table 1.

**Table 1 Particle size distribution**

Sample	D10	D30	D50	D60	D80
Un-neutralised leach residue	3	16	43	61	116

### 2.2 Specific gravity

The specific gravity of the leach residue was measured according to ASTM D854-06 (1998) and the average specific gravity was measured as 3.00.

### 2.3 Mineralogical analysis

The mineralogical analysis of the leach residue was performed using XRD Techniques. Computer analysis of the XRD patterns provides the semi-quantitative mineralogical composition of the sample. The results are presented in Table 2.

**Table 2** Semi-quantitative mineralogical composition of un-neutralised leach residue

Mineral SQ-XRD	Composition (%)
Albite	42
Muscovite	55
Quartz	22
Gypsum	11

## 2.4 Chemical analysis of leach residue and leach solution

The chemical analyses of the leach residue and leach solution (supernatant) were performed using XRF and ICP-MS techniques, respectively. The results are shown in Tables 3 and 4.

**Table 3** Chemical composition of leach residue

Sample	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	LOI	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Total
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Un-neutralised tails	12.2	3.44	4.04	1.5	24.51	0.91	0.28	2.87	0.74	45.57	2.37	98.42

**Table 4** Chemical composition of leach solution

Parameter	Leach Solution (mg/L)
Sulphate (SO <sub>4</sub> )	109,000
Silicon (Si)	471
Aluminum (Al)	8,130
Antimony (Sb)	0.015
Arsenic (As)	60.7
Barium (Ba)	0.031
Beryllium (Be)	0.26
Cadmium (Cd)	13
Chromium (Cr)	31
Cobalt (Co)	14
Copper (Cu)	11
Iron (Fe)	24,100
Lead (Pb)	0.16
Manganese (Mn)	1,960
Molybdenum (Mo)	1.51
Nickel (Ni)	3.82
Selenium (Se)	3.13
Silver (Ag)	0.002
Strontium (Sr)	41.6
Thallium (Tl)	0.10
Tin (Sn)	0.62
Titanium (Ti)	26.3
Uranium (U)	1,400
Vanadium (V)	37
Zinc (Zn)	281

The sample contained very little supernatant. In the current sample over 90% of the water appeared to be bond to the solids as a gel-like mass. Based on the average grade of the ore and a quick mass balance around the dissolved uranium in solution, it appears that the water bond within the solids matrix would be similar to that of the supernatant.

As for the mineralogical make up of the solids the sample contained muscovite (Mica) (25% by weight) and chlorite (9% by weight). The presence of muscovite (mica) due to its platy nature would negatively affect settling and dewatering properties of tailings. There was also gypsum (11% by weight) in the leach residue.

Since the leach residue needs to be dried prior to being subjected to XRD, the presence of large quantities of dissolved elements in the solution trapped within the solids matrix (due to the 'gelling' observed) could lead to the formation of secondary minerals. This would occur as the water in the sample evaporates and the solubility of the dissolved elements is exceeded.

### 3 Experimental procedure and results

Three sets of tests were conducted including the neutralisation of: leach solution (i.e. tailings supernatant); leach slurry (i.e. tailings); and sequential neutralisation on leach slurry to be able to assess possible separate formation and selective separation of gypsum from the neutralisation precipitates. In addition, for comparison purposes, thickening of the material by a deep bed paste thickener and filtration of the material as received and after controlled neutralisation were tested. The products generated from the straight neutralisation and controlled neutralisation processes were compared for final volume, filterability and the resulting water quality.

#### 3.1 Controlled neutralisation (gypsum crystal growth)

The initial test work for the assessment of the controlled neutralisation process was performed using the supernatant (leach solution) that had collected on top of the leach tailings. As previously discussed this represents only a fraction of the solution contained within the sample.

The test work involved adding dry hydrated lime to the supernatant, raising the pH and forcing the precipitation of gypsum and metal hydroxide solids. Air was also added to oxidise the iron to its less soluble and chemically more stable ferric state. Solids precipitated from this first stage are typically finely divided particles. In order to improve the size of these precipitates, they are recycled (i.e. reintroduced) with lime in a second sample of supernatant. The precipitates from this first stage serve as seeds for the fresh solids being formed. Thus newly precipitated solids grow on top of old particles, forming much larger crystals that settle more rapidly and to a higher final density. It would also improve the dewatering (filterability) properties. With each stage of recycling, the volume of precipitates (sludge) decreases, indicating a higher final density. The results are summarised in Table 5. No attempt was made to optimise the final density and this would need to be included as part of a more detailed testing program.

**Table 5 Sludge densification from controlled neutralisation**

<b>Volume of Leach Solution (ml)</b>	<b>Sludge Volume (without Controlled Neutralisation) *</b>	<b>Sludge Volume (with Controlled Neutralisation)</b>	<b>Reduction in Volume (%)</b>
50	125	125	0
+ 50 (100)	250	210	16
+ 50 (150)	375	300	20
+ 50 (200)	500	350	30
+ 50 (250)	625	400	36

Note: \* Does not take into account consolidation that would take place with a thicker sludge bed

Another beneficial aspect of the controlled neutralisation is the improvement in water quality resulting from the neutralisation process. As can be seen in Table 6, the amount of sulphate in the water that could be recycled is further reduced when control neutralisation is used. At about 2,000 mg/L sulphate concentration would be at or close to its solubility limit and would therefore greatly reduce the amount of gypsum scaling that could occur on full scale once the mill is in operation.

**Table 6 Summary of water quality of neutralisation of leach solution**

<b>Parameter</b>	<b>Leach Solution Supernatant (mg/L)</b>	<b>After Straight Neutralisation (mg/L)</b>	<b>After Controlled Neutralisation (mg/L)</b>
Sulphate (SO <sub>4</sub> )	109,000	2,470	2,200
Silicon (Si)	471	0.36	0.24
Aluminum (Al)	8,130	2.61	2.15
Antimony (Sb)	0.015	<0.0002	<0.0002
Arsenic (As)	60.7	11.2	10.9
Barium (Ba)	0.031	0.0056	0.0063
Beryllium (Be)	0.26	<0.0001	<0.0001
Cadmium (Cd)	13	0.0006	0.0011
Chromium (Cr)	31	0.0007	0.0007
Cobalt (Co)	14	0.0003	0.0009
Copper (Cu)	11	0.0008	0.0095
Iron (Fe)	24,100	0.17	0.56
Lead (Pb)	0.16	<0.0001	0.0001
Manganese (Mn)	1,960	0.48	1.37
Molybdenum (Mo)	1.51	0.128	0.009
Nickel (Ni)	3.82	0.0005	0.0025
Selenium (Se)	3.13	0.0008	0.0008
Silver (Ag)	0.002	<0.0001	<0.0001
Strontium (Sr)	41.6	0.66	0.72
Thallium (Tl)	0.10	0.018	0.021
Tin (Sn)	0.62	0.0004	0.0003
Titanium (Ti)	26.3	0.0005	0.0007
Uranium (U)	1,400	1.99	4.24
Vanadium (V)	37	0.0007	0.0013
Zinc (Zn)	281	0.0056	0.012

The test results were reproduced at five times scale up tests and resulted similar lime requirements as approximately 242 g/L lime.

### 3.2 Leach slurry

The testing program was limited to the supernatant, however due to the encouraging results obtained on the leach solution, additional testing on the leach slurry was also performed. The same approach was taken as for the leach solution. This additional testing indicated that on a volume basis more lime was required to neutralise the slurry even though it contains proportionately less solution by volume. The lime requirements were as follows:

- Leach solution: 242 to 244 g of hydrated lime/litre of solution.
- Leach slurry: 289 to 307 g of hydrated lime/litre of slurry.

These results indicate that there would be other reactions taking place during the neutralisation of the slurry that are not occurring during the neutralising of the leach solution (supernatant). To better understand the process mechanisms additional testing would be required.

During testing the change of colour from green to orange/brown was observed which took over four hours. It was also noticed that at a pH of between 4 and 5, the material becomes very stiff. The material softened and became easier to dewater at a pH between 6 and 7. As lime addition continues to increase the pH, the material became softer. At a pH of between 9 and 10, the material starts to thicken again.

Based on the results obtained using straight neutralisation tailing density is predicted to be around 35 wt% solids compared to the 48.9 wt% presented in the uranium process flow sheet developed. The material produced from the straight neutralisation process could not be dewatered further by either filtration or compaction in a thickener. With controlled neutralisation, especially if vacuum filtration, is applied current preliminary testing indicates that 50 wt% solids or higher could be obtained in full scale. In addition to the increased wt% solids in the resulting neutralised tailings, the controlled neutralisation improves dewaterability properties of the materials.

### **3.3 Sequential neutralisation (potential for selective separation of gypsum)**

The objective was to examine the possibility of producing a gypsum cake separately from the metal hydroxide precipitates using sequential neutralisation. While no attempt was made to optimise the process, it appears there is the possibility of producing a fairly clean (low metals content) gypsum cake. In addition, removing the gypsum could help increase the UCS strength of cemented neutralised tailings. Depending on the final metal content it could also be a useable gypsum product (e.g. marketable, liner material, etc.). Based on the current preliminary test results if the gypsum cake could be recovered there is the possibility of reducing by up to 30% (250 ml/850 ml) the amount of sludge going to the tailings management facility. Selectively separated gypsum could be used as an additive somewhere else. It has been reported that the presence of gypsum in backfill material could cause reduction in compressive strength of the backfill material. Selective separation of gypsum from tailings before preparation of the backfill material could improve the strength. Testing would be required to confirm and develop a suitable process.

### **3.4 Sequential deep bed paste thickener**

There was not enough material to allow the testing of the neutralised tailings (either from conventional or controlled neutralisation). However, testing was performed on the un-neutralised tailings to assess the possible benefits of using a paste thickener. Testing the un-neutralised tailings would have the added benefits, if the leach slurry could be dewatered close to that of a paste consistency before neutralisation, of reducing the amount of gypsum in the tailings which could possibly result in higher strength backfill.

Based on the current settling and dewatering test results it was possible to increase the wt % solids from 40 to 46 wt%. Going from 40 to 46 wt % solids for a material with a specific gravity of 3.0 would reduce the amount of water in the tailings by approximately 12.5%. Since the filterability and cake loading of the leach residues improved using controlled neutralisation there is the possibility for further gains in density and water recovery. This would need to be confirmed via additional testing.

Due to the limited amount of supernatant, water acidified to a pH of 1 using sulphuric acid was used. The result was the dilution of the water used in the test work (supernatant and bond in the solids matrix gel) by a factor of approximately three. The thickener overflow is the solution that was used for the sequential neutralisation (gypsum) recovery test work.

### **3.5 Unconfirmed compressive strength (USC) test**

Typically cemented paste backfill is produced with a material with a slump between 250 and 175 mm in order to minimise binder requirements and allow for a material that is pumpable. Based on the rheological test work performed on the un-neutralised leach residue this slump range would require a material between 61 to 64 wt% solids. The lab scale paste thickener achieved 46 wt%. However neutralising the paste thickener underflow to a pH of 10 using dry hydrated lime produced a material with a slump less than 175 mm. Water was reintroduced to adjust the material to a 175 mm slump material before the cylinders were cast with 5 wt% Portland cement. To test the effect of the gypsum precipitates, additional samples were

cast with 10% by weight of gypsum sludge generated during the neutralisation test work on the leach solution.

The samples achieved very low strength reaching only 60 kPa after 28 days. The samples with the extra gypsum were even lower at 25 kPa. Typically with tailings for instance, in the order of 250 kPa strength are achieved with 5 wt% binder to prepare backfill material. While neutralising the sample to pH 7, rather than 10, would reduce the amount of gypsum, until higher densities can be achieved by conventional dewatering it is not worth while considering paste backfill as a viable option.

## 4 Conclusions and recommendations

The tests conducted on the acid leach solution and acid leach slurry to evaluate the effect of controlled neutralisation process indicated that possibly gypsum has been precipitating and forming crystals and with several recycles and prolonged time in the process the crystals grow to positively affect the dewatering properties of the neutralisation product. Controlled neutralisation greatly reduced the volume of neutralisation precipitates which typically results in a higher final density and wt% solids. Additionally it showed improved dewatering (filtration) properties. Controlled neutralisation also reduced the amount of sulphate in solution close to that of its saturation limit, which would reduce the amount of scaling that occur during full scale application. Additional testing was performed to ascertain if the controlled neutralisation would work efficiently on the leach slurry as well. It was observed from these preliminary tests that the dewatering properties (filterability) of the neutralised material could improve. These preliminary results indicate that this technology could work, however additional tests on a larger scale would be required to verify these results.

Deep bed paste thickener improved the final wt% solids of the underflow. The test work on the un-neutralised leach slurry demonstrated that it was possible at the bench scale level to improve final density and recover additional water. From the final density observed as part of the current test work, without any scale up, in the order of 10 to 15% of extra water could be recovered.

Unconfined compressive strength (UCS) tests performed on thickened un-neutralised slurry neutralised with hydrated lime to a pH of 10 did not provide sufficient strength to warrant further studies at this time. Testing did demonstrate however that reducing the amount of gypsum gave better results. If the amount of gypsum could be reduced or the final wt% of the neutralised tailing increased to give a paste with a measurable slump (defined by Golder PasteTec as < 250 mm) using controlled neutralisation process, a few additional exploratory cylinders should be cast. As it currently stands, cemented rock fill could be the better alternative for producing a suitable underground backfill for use on the project.

As future tests, the strength of slump produced from controlled neutralisation process should be tested to determine whether paste backfill could be a viable option. It is also important to investigate the sample tested is representative of uranium ore in composition.

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