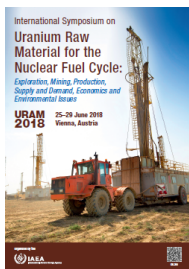


International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle: Exploration, Mining, Production, Supply and Demand, Economics and Environmental Issues (URAM-2018)



Contribution ID: 123

Type: ORAL

HYDROMETALLURGICAL CONTROLS ON ARSENIC, MOLYBDENUM AND SELENIUM IN URANIUM MILL EFFLUENT AND TAILINGS

Thursday, 28 June 2018 10:20 (20 minutes)

INTRODUCTION

Contamination of groundwater and surface water by arsenic, molybdenum and selenium derived from both natural and anthropogenic sources is an issue of global concern. Uranium-bearing ore material often contains all three of these elements of concern. Sulphuric acid leaching of these ores results in liberation of arsenic, molybdenum and selenium. In the hydrometallurgical process for uranium purification and concentration these elements must be separated from uranium either via solvent extraction or ion-exchange processes to achieve the required product quality for uranium ore concentrate. Often, these elements are of little or no economic value to the operator. As a result, arsenic, molybdenum and selenium are treated with the waste streams and must be removed prior to re-using the water in the process (to avoid a circulating load) or release of treated effluent to the receiving environment.

As, Mo and Se (among other elements and radionuclides) removed from the uranium mill process waste water are often combined with the mill tailings and the final mill tailings are ultimately emplaced in engineered tailings management facilities. It is imperative that the precipitated As, Mo and Se are geochemically stable and do not dissolve in the tailings management facility as transport of As, Mo or Se from the tailings facility to the local groundwater or surface water system has the potential to negatively impact the regional biota. It is therefore important for uranium processors to have well-defined and effective effluent treatment processes. In addition, the operational process must ensure geochemical stability of elements emplaced in the engineered tailings management facility.

DESCRIPTION

The Key Lake uranium mill is located approximately 650 km north of Saskatoon, Saskatchewan, Canada. The climate is sub-arctic with a mean annual temperature of 4 °C (ranging from -45 to 25 °C) [1]. The mill is located within the Athabasca Basin which contains the world's richest uranium deposits. The Key Lake mill began production in 1983 and two open pit mines were mined from 1983 to 1997. Stockpiled ore continued to feed the mill from 1997 to 1999 and in 1999 the Key Lake mill began to receive ore from the McArthur River mine located approximately 80 km to the north of the Key Lake mill [2].

The Key Lake mill blends the high-grade ore from the McArthur River mine (~18% U₃O₈ wt/wt) with low grade (~0.2% U₃O₈ wt/wt) material stockpiled at the Key Lake uranium mill. The resulting leach feed slurry head grade is about 5% U₃O₈. Leaching of the leach feed slurry takes place in agitated leach tanks where sulfuric acid and oxygen are added along with steam. Retention time is approximately 24 hours and the resulting uranium recovery averages 99.2%.

Following the leaching process the undissolved sandstone material is separated from the leach aqueous solution in a series of eight thickeners. Acidic wash water is introduced in a counter current fashion to wash adsorbed uranium from the leach residue solids. This occurs at each stage of thickening. The resulting leach aqueous solution is then fed to the solvent extraction (SX) circuit where the uranium is purified and concentrated. The resulting purified and concentrated uranium-bearing loaded strip solution is then forwarded to the yellowcake precipitation circuit where the uranium is precipitated as ammonium diuranate. The ammonium

diuranate precipitate is thickened, washed, dewatered and then calcined at 850 °C to produce a jet-black free flowing uranium oxide powder.

The uranium-free waste aqueous solution from the SX process (raffinate) contains the dissolved metals (including As, Mo, Se) and radionuclides liberated in the leaching process. This solution is forwarded to the effluent treatment process and mixed with other process waste waters. The mixture of waters is progressively neutralized with lime in a series of four pachucas with target pH of 1.2, 3.5, 6.5 and 9.5 [3]. Barium chloride is also added at the second stage of neutralization to co-precipitate Ra-226 as Ba/Ra-SO₄. The chemical precipitates formed in this neutralization series are settled in a thickener. The overflow solution is pH adjusted with dilute acid to a target pH of 6.2. The solution is forwarded to a final clarifier before being transferred to monitoring ponds for analysis and certification before being released to the environment. Off-spec treated effluent is redirected to a contaminated water reservoir and reintroduced to the effluent treatment circuit for reprocessing.

This effluent treatment scenario resulted in removal efficiency for As, Mo and Se of 99.8%, 21% and 19%, respectively. Correspondingly, the average daily concentration of As, Mo and Se in the Key Lake mill final effluent was 0.006 mg/l (n=81; Range = 0.003 to 0.017 mg/l; Standard Deviation = 0.002), 0.74 mg/l (n=81; Range = 0.27 to 1.8 mg/l; Standard Deviation = 0.27) and 0.073 mg/l (n=81; Range = 0.052 to 0.094 mg/l; Standard Deviation = 0.010), respectively. This resulted in average annual loadings of As, Mo and Se of 9 kg/y, 1,110 kg/y and 110 kg/y, respectively to the downstream receiving environment.

Environmental studies in the downstream receiving environment of the Key Lake mill effluent concluded that Mo and Se could have an impact if loading of these elements to the lake sediments was not reduced. Arsenic, at the annual current loading, was determined to not be having an impact on the downstream receptors. The environmental studies further concluded that if annual loadings of Mo and Se remained below 600 kg and 40 kg respectively, the long-term impact would be reduced to a level that was in keeping with the original environmental impact statement for the Key Lake mill. Therefore, technical and operations personnel were required to enhance the current effluent treatment process to increase the removal efficiency of Mo and Se while at the same time not increasing the loading of As (or other elements of concern) to the environment.

In an effort to increase the removal efficiency of Mo and Se and subsequently reduce the concentrations of the elements in the mill final effluent several treatment options were evaluated and tested. These options included:

- Reverse osmosis
- Ion exchange
- Co-precipitation of oxy-anions with ettringite
- Reduction and adsorption with zero valent iron
- Microbial reduction
- Photocatalytic reduction using UV Light and TiO₂
- Adsorption of oxyanions to ferrihydrite followed by gypsum encapsulation

The criteria for testing and ultimately selecting a treatment option included the following:

- The selected option must integrate well with the current processing infrastructure
- Must be capable of achieving the desired targets on a consistent basis
- It must not increase the concentration of any other regulated/non-regulated element in the mill final effluent
- It must be robust and circuit availability (uptime) must not be affected (currently was at 95% uptime)
- Capital and operating costs must be considered when selecting a final option.

DISCUSSION

The above noted seven treatment options were evaluated and tested based on the criteria identified. A brief summary of the results of each treatment option is summarized below.

1. Reverse osmosis

Reverse osmosis was considered as a processing option to remove As, Mo and Se from the mill effluent. Results showed that the high concentration of Ca and SO₄ in the effluent (near saturation) feeding the RO system resulted in significant scaling and rapid fouling of the RO membranes. As a result this technology was not considered any further.

1. Ion exchange

Ion exchange resins were tested for their affinity for As, Mo and Se. In all cases the high ionic strength of the mill effluent (saturation with respect to Ca and SO₄) resulted in scaling of the column and resin beads and also resulted in excessive back pressure on the column. This caused flow restrictions in the IX columns in all resins tested. As a result this technology was not considered further.

1. Co-precipitation of oxy-anions with ettringite

Ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3$) precipitates from solutions containing Al, Ca and SO_4 at high pH levels (pH >11) [4]. Selenium (as selenite or selenate), arsenic (as arsenite or arsenate) and molybdenum (as molybdate) can substitute SO_4 in the ettringite lattice thereby removing these elements of concern from solution. Results from testwork showed that Se was removed solution but not to the level required. Removal efficiencies for As and Mo were not improved with this chemical treatment process. Finally, to effectively precipitate ettringite the addition of aluminum was required at stoichiometric levels and this resulted in an increased in the concentration of aluminum in the mill final effluent. This was not acceptable as Al in the effluent can have a negative impact on downstream receptors. As a result this technology was not considered any further.

1. Reduction and adsorption with ferrous iron or zero valent iron (ZVI)

Test work results showed that selenium removal improved when ferrous sulphate (“green rust”) was added to the water stream at pH 4. However this option was not pursued further due to excessive sludge levels to tailings, high reagent costs when compared to marginal process performance improvement. ZVI iron in the form of iron filings was also tested on a bench scale, again yielding marginal improvement and was observed to be prone to surface passivation.

1. Microbial reduction

The use of microbes to electrochemically reduce As, Mo and Se to elemental form thereby significantly reducing the concentration of these elements of concern in the final effluent combined with a geochemically stable species in the mill tailings was evaluated. Results showed that it was difficult to sustain the biomass as it was sensitive to changes in temperature and redox conditions. Further, traces of SX organic carry over in the raffinate also had a detrimental effect on the biomass. Results further showed that these aspects would cause a rapid deterioration in the biomass and it took several days for the biomass to recover. Should this happen at the plant scale, if the process were to be implemented, the resulting mill final effluent has the potential to be off-spec with respect to Mo and Se for several days while the biomass stabilized. This was unacceptable from a process perspective. As a result this technology was not considered any further.

1. Photocatalytic reduction using UV Light and TiO_2

Photo-assisted electrochemical reduction of oxyanions (e.g. As, Mo and Se) using semiconductor particles as catalysts was investigated. Of all semiconductors, titanium dioxide is suited for photocatalytic processes [5-7]. Titanium dioxide is highly stable, non-toxic and has the potential to be reused following its recovery from the treated effluent stream. The ability of titanium dioxide to function as a photocatalyst arises from its semiconducting properties. Illumination of semiconductor particles with electromagnetic radiation (e.g. UV light) of energy greater than their band-gap results in the promotion of an electron from the valence band (VB) to the conduction band (CB). This process generates pairs of electrons (e^-) and holes (h^+) in the CB and VB, respectively. The CB becomes electron-rich, and hence possesses a reducing ability while the VB hole is deficient of electrons thereby possessing an oxidizing ability [12]. Titanium dioxide has an adsorption affinity for oxidized oxyanions. In the context of Se(IV) or Se(VI) reduction, the electromagnetic radiation produced CB electrons are transferred to either the adsorbed Se(IV) or Se(VI) species, reducing them to elemental Se. The same mechanism was hypothesized for As and Mo oxyanions in solution.

Results on clean distilled water spiked with As, Mo and Se (as AsO_4^{3-} , SeO_4^{2-} and MoO_4^{2-}) showed excellent results for Se removal with >99% of the Se converted to elemental Se. Removal efficiencies for As and Mo were lower (10% and 15%). This was attributed to a lower adsorption affinity of TiO_2 for As and Mo oxyanions. The application of photocatalytic reduction using UV light and TiO_2 was also tested on Key Lake mill effluent. Results showed significantly reduced removal efficiencies for As, Mo and Se as compared to results achieved with spiked clean distilled water. Removal efficiencies of 48%, 5% and 7% were observed for Se, As and Mo, respectively. The difference was the reduced photon flux from the UV light in the mill effluent sample due to the higher total dissolved solids concentration. Based on these results and limited commercial plant-scale applications this technology was not considered any further.

1. Adsorption of oxyanions to ferrihydrite followed by gypsum encapsulation

Dissolved iron in solution forms two-line ferrihydrite at pH 3.2 and has a strong adsorption affinity for As, Mo and Se oxyanions in solution due to the net positive surface charge of ferrihydrite at this pH [8-9]. Test work completed on mill effluent showed very good removal efficiency of As, Mo and Se over the pH range 3.5-4.5. The target pH of the mill final tailings is pH 11 and the surface charge of ferrihydrite changes from net positive to net negative above pH 8.1, thereby desorbing As, Mo and Se. Pre-neutralizing the adsorbed Fe-As/Mo/Se complex from pH 4.5 to 7.5 using lime increased the geochemical stability of this complex when it was mixed with the final tailings at pH 11. Aging studies confirmed that this adsorption complex combined with gypsum encapsulation at pH 7.5 resulted in a stable complex within the tailings management facility. Based on these positive results the Key Lake mill effluent treatment circuit was modified to include enhanced Eh control, a low pH (pH 4.5) thickener and a gypsum encapsulation tank.

RESULTS ACHIEVED

The selected ferrihydrite precipitation hydrometallurgical treatment method achieved excellent results at full plant scale. Prior to the installation of the required process equipment and subsequent process changes the daily concentrations of As, Mo and Se in the mill final effluent were as follows: As average concentration = 0.006 mg/L (n = 81; Range = 0.003 mg/L to 0.017 mg/L; Standard Deviation = 0.002). Mo average concentration = 0.74 mg/L (n = 81; Range = 0.27 mg/L to 1.8 mg/L; Standard Deviation = 0.27). Se average concentration = 0.073 mg/l (n = 81; Range = 0.052 mg/l to 0.094 mg/l; Standard Deviation = 0.010).

After the installation of the thickener the average daily concentration of As, Mo and Se were as follows: As average concentration = 0.005 mg/L (n = 145; Range = 0.001 mg/L to 0.019 mg/L; Standard Deviation = 0.003). Mo average concentration = 0.10 mg/L (n = 145; range = 0.005 mg/L to 0.70 mg/L; Standard Deviation = 0.086). Se average concentration = 0.018 mg/L (n = 145; Range = 0.004 mg/L to 0.031 mg/L; Standard Deviation = 0.004).

As a result of these changes to the effluent treatment circuit the removal efficiency for As remained high and was 99.8% before process changes and 99.9% following the changes. Significant improvement was observed for Mo and Se where the removal efficiencies increased from 21% to 90% for Mo and from 19% to 80% for Se. Finally the annual loading of Mo and Se to the environment decreased from 1,110 kg/y to 100 kg/y for Mo (on average) and from 110 kg/y to 18 kg/y (on average) for Se. Finally, following implementation of the effluent treatment process improvements, the Key Lake mill met environmental performance expectations (as per the environmental impact statement) with respect to effluent quality. The annual loadings for Mo and Se after process improvements were below the limit of 600 kg/y for Mo and 40 kg/y for Se.

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Session Classification: Tailings and waste management

Track Classification: Track 11. Tailings and waste management