

Mineralogical controls on Uranium hydrogeochemistry from mine wastes

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Abstract: Uranium mining creates several geochemically complex waste products. The complexity arises from the wide variation in deposit types, mining methods, ore processing methods, and waste disposal methods. However, a number of geochemical tools can be applied to the problem of predicting water quality impacts from uranium mining. This paper presents examples of the use of geochemical methods to predict the water quality associated with uranium mine waste rock and tailings.

1 INTRODUCTION

In the past five years, the authors have participated in geochemical investigations at over a dozen uranium mines in North America, Europe, and Africa. Despite the wide variety of ore deposit types, mining methods, processing methods and waste disposal methods, the tools of conventional (and not so conventional) geochemistry have been productively applied to all of the problems encountered. This paper presents examples of the application of geochemical tools to the investigation of wastes created by past and current uranium mining. Although geochemical methods are also used in investigations of ore deposit genesis, in directing exploration programs, and in refining metallurgical processes, the primary focus herein is on managing the impact of mine wastes on water quality.

2 URANIUM MINING OVERVIEW

To understand the complexity of uranium mine waste geochemistry, it is useful to have a brief overview of the industry. The complexity starts with the wide range of uranium deposit types that have been or are being mined. A detailed review of uranium geology is not possible here. Suffice to say the number of deposit types has historically increased at least as quickly as the number of known deposits. For example, a 1971 text on uranium processing listed ten deposit types that were in production at the time (Merrit, 1971), while a 1978 short-course handbook on uranium deposits contained fifteen chapters describing various deposit types and their genesis (Kimberly, 1978).

Over half of the world's current production is from so-called "unconformity-type" deposits. These deposits were typically formed between 1800 Ma to 1200 Ma, after atmospheric oxygenation led to the dissolution and transport of

hexavalent uranium as the uranyl ion (UO_2^{++}). The unconformity-type deposits are spatially, and probably genetically, related to paleo-weathering surfaces (Marmont, 1988). But even within this one deposit type, there is a variety of ore minerals resulting from (arguably) a variety of genetic processes. As discussed below, accessory minerals present in the ore and surrounding waste rock further complicate the story.

A variety of methods are used to extract the ore. Current uranium production (western world only) is approximately 35,000 tonnes U per year. The ten largest mines, listed in Table 1, produce over 70% of that total. Open-pit and underground uranium mines account for nearly 80% of production (about 40% by each method). Production of uranium as a by-product from copper or gold mines contributes another approximately 10%. Slightly more than 10% of current production comes from in situ leaching of uranium deposits. (Uranium Institute, 1998)

Table 1 Ten largest uranium mines (1997 data from Uranium Institute)

Mine	Country	Mine Type	1997 Productions (tonnes U)
Key Lake	Canada	Open pit	5433
Rabbit Lake	Canada	Underground	4632
Ranger	Australia	Open pit	4095
Rossing	Namibia	Open pit	2905
Akouta	Niger	Underground	2139
Cluff Lake	Canada	O/P and U/G	1964
Olympic Dam	Australia	Byproduct	1425
Arlit	Niger	Open pit	1358
Vaal Reefs	South Africa	Byproduct	677
Highland	U.S.A.	In situ leach	597

The mining method has a significant impact on the amount of waste rock that is produced. Open pit operations at the Key Lake Mine, for example, have produced over 70 million tonnes of waste rock that now covers over 150 ha. Even underground mining can produce significant quantities of waste, particularly from low grade deposits such as those that were previously mined in the former East Germany. (Hockley and Holl, 1995)

Processing of uranium ores at mine sites generally includes:

- crushing and grinding,
- leaching with a strong oxidant and acid or, less commonly now, with carbonate,
- separation of leached solids from the uranium-bearing raffinate (commonly in a countercurrent decantation system),
- extraction and concentrate of the uranium from the raffinate (by ion exchange or solvent extraction with strong acid or salt stripping),
- precipitation of uranium,

- drying and heating to produce a “yellowcake” containing 70-80% by weight of uranium oxides. (Uranium Saskatchewan, 1994)

The ore processing has a significant effect on the amount and type of tailings that are produced. Unlike tailings from many other mineral processing operations, uranium tailings contain more than just residues of the ground and leached ore. A significant proportion of the solids going to a uranium tailings impoundment consists of gypsum and iron hydroxide sludges generated during neutralization of the leach residues. Sludges generated by neutralization of excess raffinate can also be an environmentally important component, due to the high concentration of metals and radionuclides. It is also common at many mines to bring smaller waste streams, such as minewater and excess or spent extraction solutions, into the tailings stream.

Finally, methods of waste disposal vary significantly from one site to another, and even at the same site as new methods become available. In northern Saskatchewan, for example, uranium tailings have been deposited in natural water bodies, in engineered surface impoundments, in mined out pits, and in pit lakes. In the former East Germany, waste rock was used as underground backfill, or disposed on surface, and current remediation methods include backfilling the waste rock into open pits, relocating and consolidating waste rock piles, and construction of soil covers. Obviously, the disposal method can have significant effects on the environmental geochemistry of the waste. In fact, most modern waste disposal methods are designed to minimize geochemical instability and the resulting potential for degradation of water quality.

3 APPLICATIONS OF GEOCHEMICAL METHODS TO URANIUM WASTE ROCK

3.1 Classical geochemistry and uranium solubility

Figure 1 shows pH, uranium and sulfate concentrations from over 130 column tests on waste rock samples taken throughout the former uranium mining district near Ronneburg, Germany. The data shown are from analyses of solutions that were contacted with the waste rock samples in saturated columns for one week. The column tests were continued under saturated and unsaturated conditions for up to three years, and the complete data are presented elsewhere (SRK 1996a, Hockley et al. 1997).

The pattern of high uranium concentrations at low pH reflects several factors. There is a lithological correlation between uranium and sulfide, which is certainly responsible for some of the apparent correlation between low pH, high sulfate and high uranium in the column solutions. However, there is also a mechanistic explanation that can be derived from chemical thermodynamics. Figures 2 and 3 show the relationship between sulfate concentration and the distribution of aqueous uranium species in solution. The limited complexation of sulfate with uranyl ion at sulfate concentrations of 100 ppm, typical of

groundwater, has been noted in several often-cited references (e.g. Langmuir 1979). However, the higher sulfate concentrations typical of the Ronneburg waste rock, (and sulfuric acid leaching), leads to much stronger uranyl complexation. (Figure 2 and Figure 3 are developed from thermodynamic constants presented in Langmuir 1977, for 25°C and air pressure.)

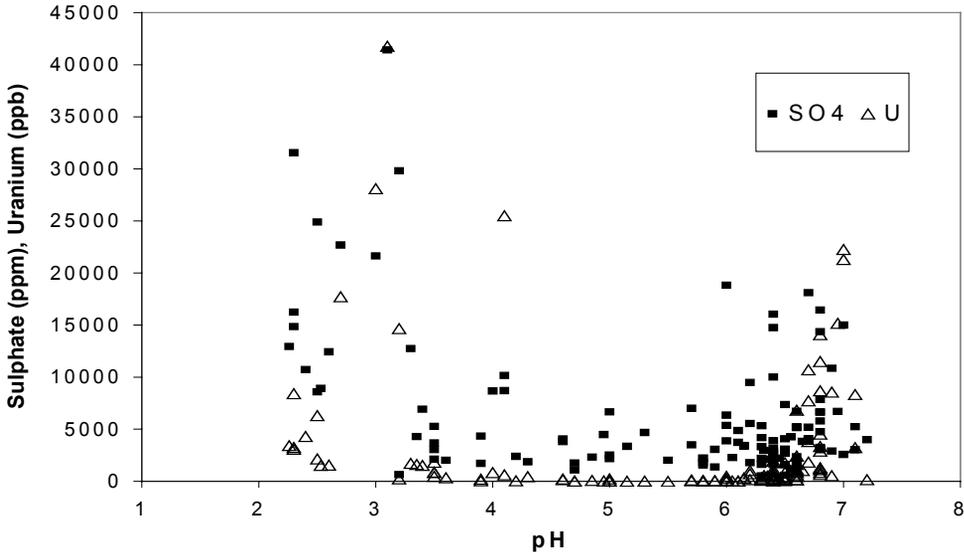


Figure 1 Uranium, sulphate and pH in column eluates from testing of Ronneburg waste rock.

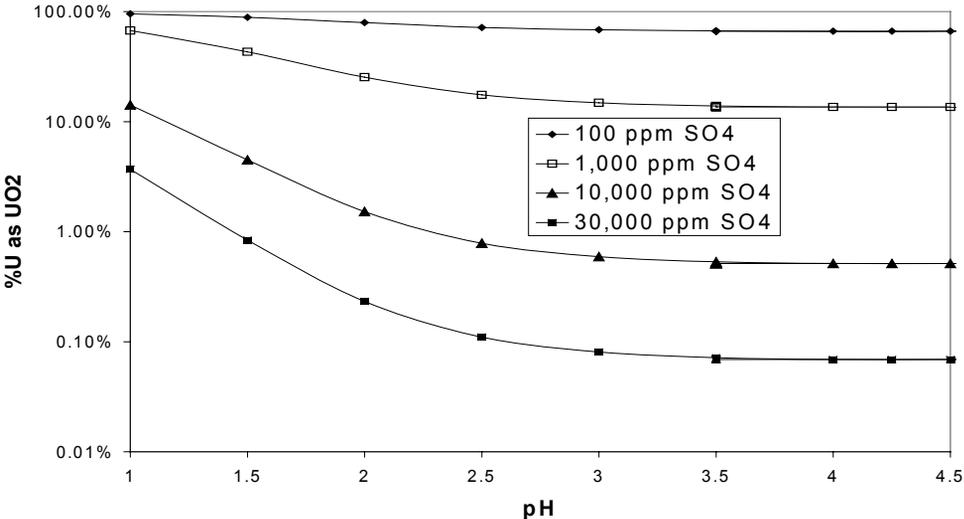


Figure 2 Percentage of soluble uranium that is in uranyl ion form, as function of pH and sulphate. Remainder of soluble uranium is in sulphate complexes

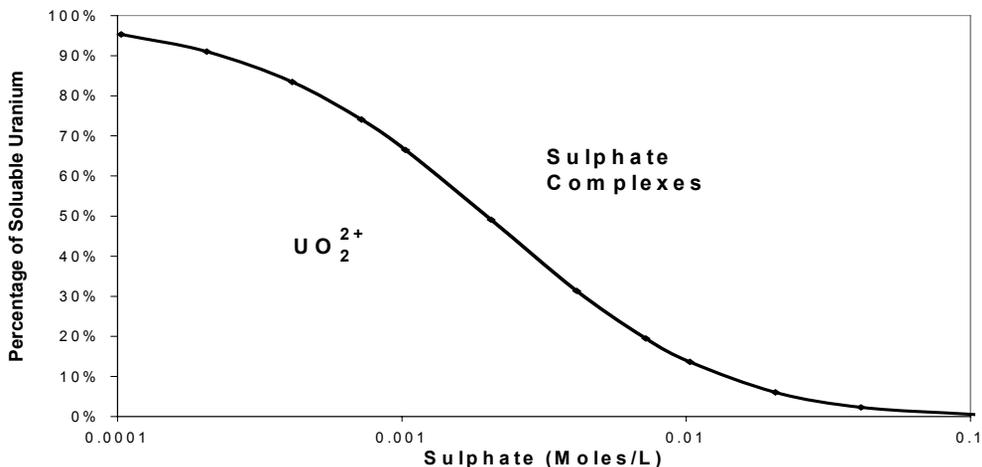


Figure 3 Uranyl ion and sulphate complexes at pH 3.5 as function of sulphate concentration.

The high uranium concentrations at neutral pH are related to the strong complexation of uranyl ion with aqueous carbonate. The carbonate complexation is well described in most standard references, and carbonate leaching of uranium was an important processing method at some historical operations, although sulfuric acid leaching is now more common. Other strong complexants of uranyl ion include phosphate and fluoride.

The Ronneburg data is discussed further below. The point here is that simple thermodynamic calculations can accurately predict trends in uranium concentrations in the presence of complexing ions. However, it should be noted that it is not always possible to accurately predict absolute concentrations of uranium in solution, due to the variable solubility of uranium mineral phases. Even the most common uranium ore mineral, uraninite, occurs in two distinct forms, i.e. crystalline uraninite and poorly crystalline pitchblende. The stability of the latter is strongly influenced by impurities (Brookins, 1988).

3.2 ARD geochemistry in uranium waste rock

Figures 4 to 6 show more data from the column tests on Ronneburg waste rock. The patterns shown are typical of acid rock drainage (ARD), a problem that is also common at many base metal and coal mines. However, there are also some trends that are not evident elsewhere. The following mechanistic explanations were developed after reviewing the site water quality monitoring data, the laboratory tests, and an extensive program of drilling and sampling of the waste rock:

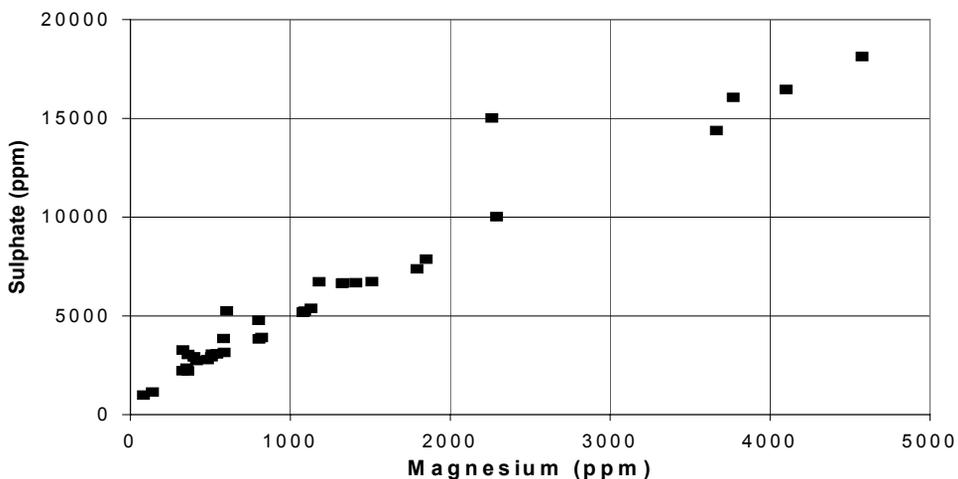


Figure 4 Correlation between sulphate and magnesium concentrations in the Ronneburg column eluates. Note, only samples with pH above 6 are shown.

- The oxidation of sulfide minerals results in the release of ferric iron, other metals, sulfate and acidity. The oxidation process is primarily controlled by the availability of oxygen (see next section).
- Dissolution of carbonate minerals results in a neutral pH and precipitation of metals. In general, neutralization reactions are rapid. When sufficient neutralizing minerals are present, complete neutralization occurs.
- When the neutralizing mineral is calcite, the calcium released reacts with sulfate to form gypsum, removing sulfate from solution. Radium-226 may co-precipitate with the gypsum. However, the high levels of carbonate in solution tend to promote uranium solubility (Figure 1, neutral region with low sulfate).
- When the neutralizing mineral is dolomite, the calcium released by the dolomite dissolution may react with sulfate to form gypsum, but the magnesium stays in solution, creating a hardness problem. Since the combination of magnesium and sulfate is very soluble, high magnesium concentrations act to support similarly high sulfate concentrations (Figure 1 neutral region with high sulfate, and Figure 4). The high sulfate concentrations tend to further enhance uranium solubility.
- When the carbonate minerals are no longer present in sufficient quantities, or when the rate of NP dissolution is hindered by surface coatings, acidic conditions develop. As the pH decreases, secondary oxide and hydroxide phases dissolve, releasing metals (Figure 5) and sorbed oxyanions (Figure 6).

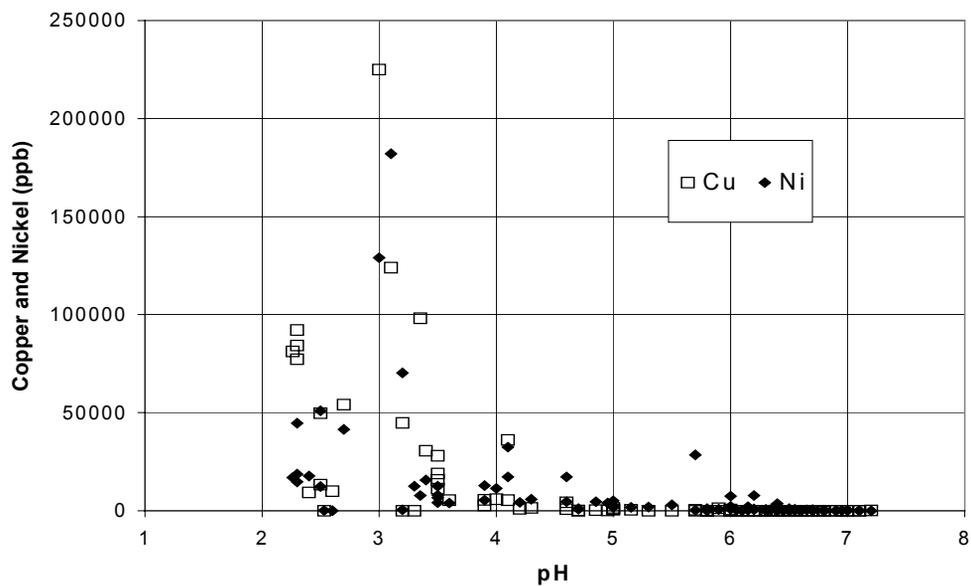


Figure 5 Copper and nickel concentrations versus pH in the Ronneburg column eluates.

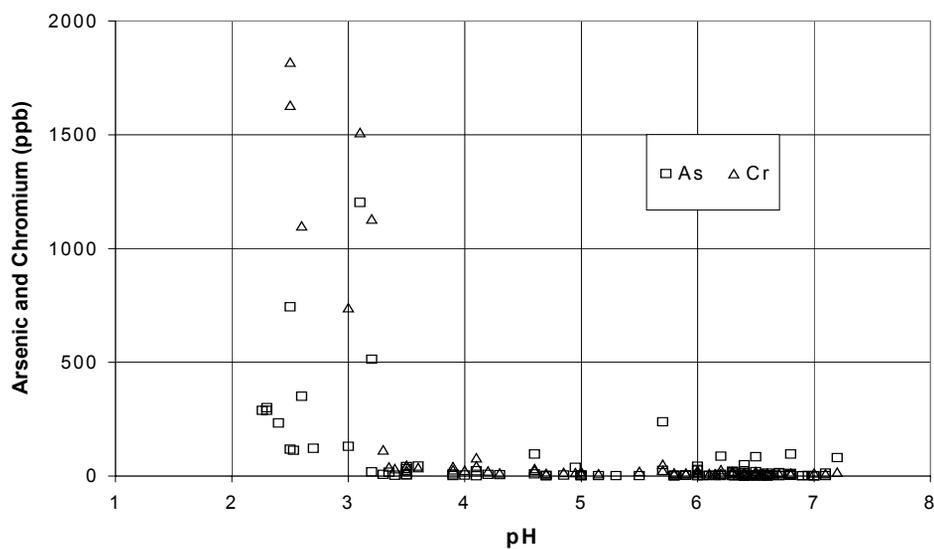


Figure 6 Arsenic and chromium concentrations versus pH in the Ronneburg column eluates.

3.3 Macroscopic influences on geochemical process in waste rock

The rate at which waste rock geochemical processes proceed is often controlled by the macroscopic processes that deliver key components to the reaction site. In fact, most waste rock remediation measures are aimed at controlling these macroscopic influences. However, it is only relatively recently that geochemical methods have been applied to the problems of macroscopic transport.

Oxygen and water are two components that must be transported to the reaction sites within a waste rock pile. SRK (1997), Lefebvre et al. (1998) and Smolensky et al. (1999) present results of an extensive program to monitor oxygen within an acidic waste rock pile known as the Nordhalde, also in the Ronneburg district. Similar programs, although with very different results, have been carried out at the Key Lake Mine (SRK 1993, Hockley and Holl 1995) and Rum Jungle Mine.

The Nordhalde program consisted of drilling eight holes into the waste rock, and inserting oxygen, temperature and pressure monitoring points. Data was collected continuously for a full year. Figure 7 shows typical results. The strong limitation on oxygen concentrations is evident. Working from the oxygen concentration profiles, it was possible to estimate rates of oxygen transport into the pile. Assuming the stoichiometry of pyrite oxidation, it was then possible to estimate rates of reaction. Since pyrite oxidation is exothermic, the temperature data could also be related to reaction rates. The reaction rates calculated from the oxygen data were independently confirmed by estimating rates of thermal convection out of the pile.

The transport of water into and through a waste rock pile is also a complex problem. SRK (1996b) noted significant releases of readily soluble salts that had apparently been stored in the waste rock. The stored salts were assumed to be indicative of incomplete flushing, probably due to flow channeling within the piles. Cumulative salt discharge and storage were estimated from historical data, and used to estimate that approximately 40% of the rock had been contacted by flow channels. That estimate is similar to literature estimates obtained by hydrologic studies (SRK, 1993).

4 APPLICATIONS OF GEOCHEMICAL METHODS TO URANIUM TAILINGS

4.1 Equilibrium modeling and mineralogy of uranium tailings

Figure 8 uses a simplified Eh-pH diagram to show the transformation of uranium ore to uranium tailings. The resulting tailings are a complex mixture of minerals that are present in the ore, minerals that are created by the acidic oxidation, and poorly crystalline, meta-stable and co-precipitated phases arising from neutralization of the leach residue and raffinate solutions. Identification of the mineral phases is a difficult problem. Especially difficult are the metastable and

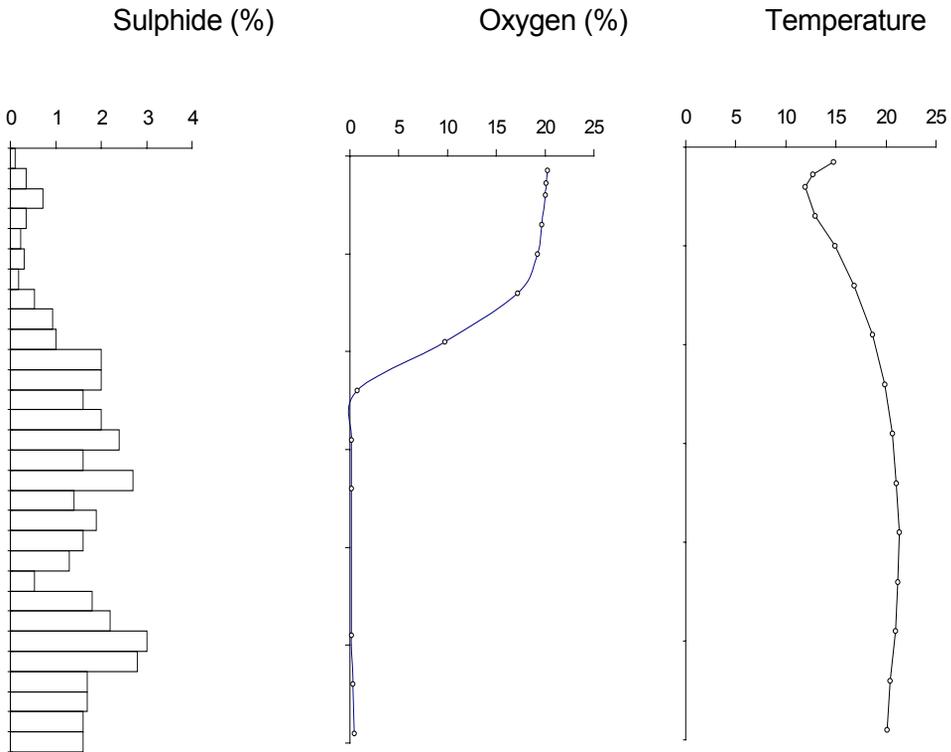


Figure 7 Results from in situ monitoring of acidic waste rock pile near Ronneburg Germany (a) Sulphide in drill cuttings. (b) September 1997 average oxygen from gas monitoring. (c) September 1997 average temperature from in situ thermistors. All profiles are 60 m.

poorly crystalline phases. The high proportions of gypsum, and the sharp peaks from the well crystallized primary minerals, make it very hard to detect the minor phases by XRD.

SRK has applied a combination of XRD, SEM, chemical analyses, and geochemical modeling to infer the presence of phases that can control the solubility of contaminants. For example, a common controlling phase in uranium mine waste appears to be a mixed Fe-Mn rich hydroxide that can host several percent of trace elements such as U as well as As, Ni and other phases (Figure 9 a-d). The method involves first attributing elements to phases that are positively identified and have a well-defined stoichiometry. If the mass balance on an element shows that some of the measured concentration remains unaccounted for, it is attributed to less crystalline phases. Solutions are contacted with the tailings and analyzed, and the results are used as input to geochemical equilibrium models to further infer the presence of possible solubility controlling phases. This combination of approaches generally allows a significant

improvement on the mineral identifications that can be accomplished with standard mineralogical techniques alone.

Recently, the method has been applied independently to constituents of the tailings, such as the neutralized raffinate, leading to even better identification of minor phases. Table 2 lists phases that have been identified and inferred in a recent series of tests (SRK 1999, unpublished data).

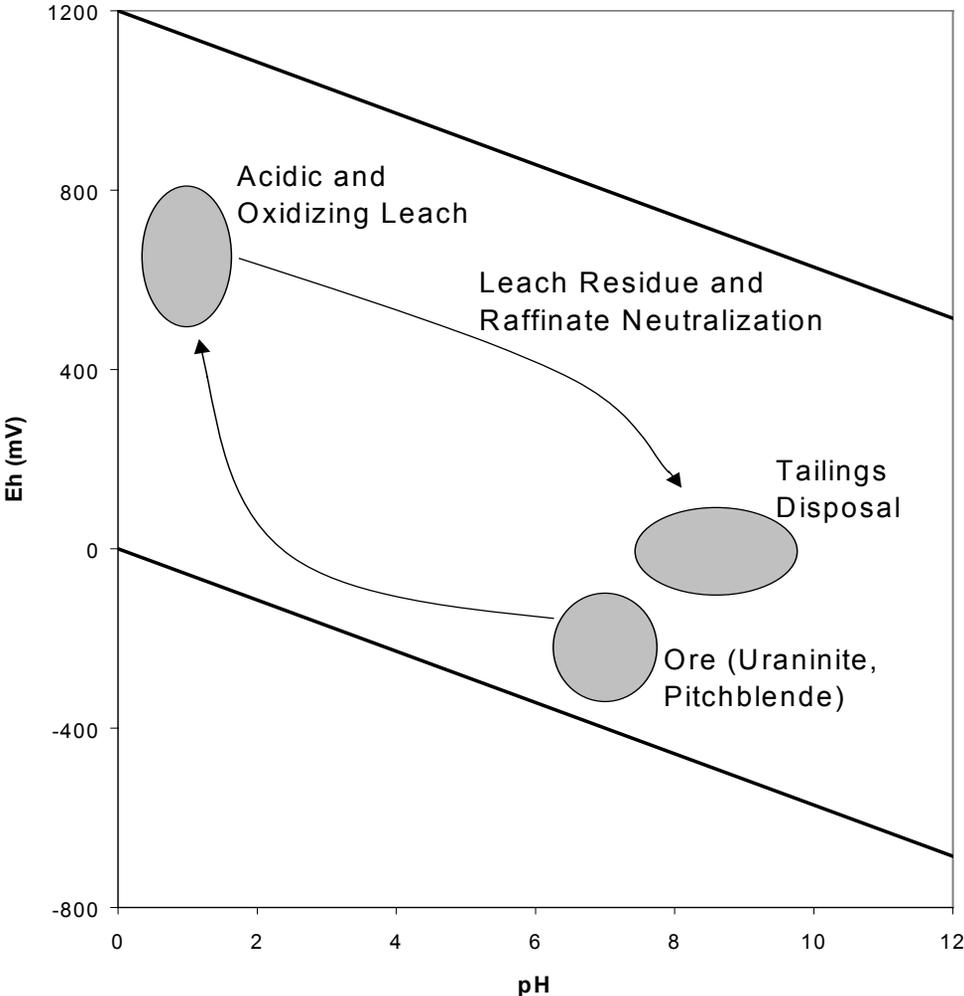
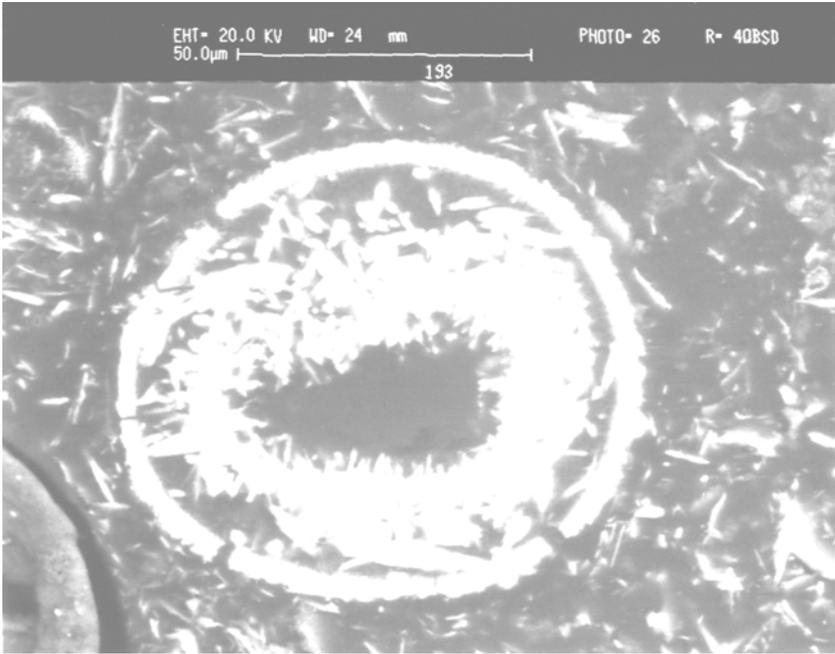


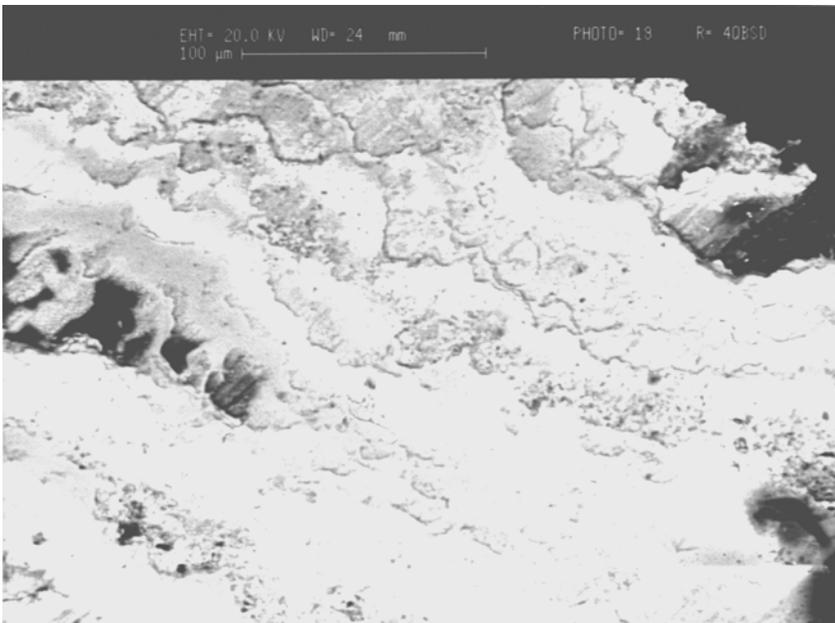
Figure 8 Eh-pH diagram showing domains that prevail during uranium ore milling and tailings disposal. (modified from Longmire et al. 1981)

4.2 Radionuclides and tailings disposal

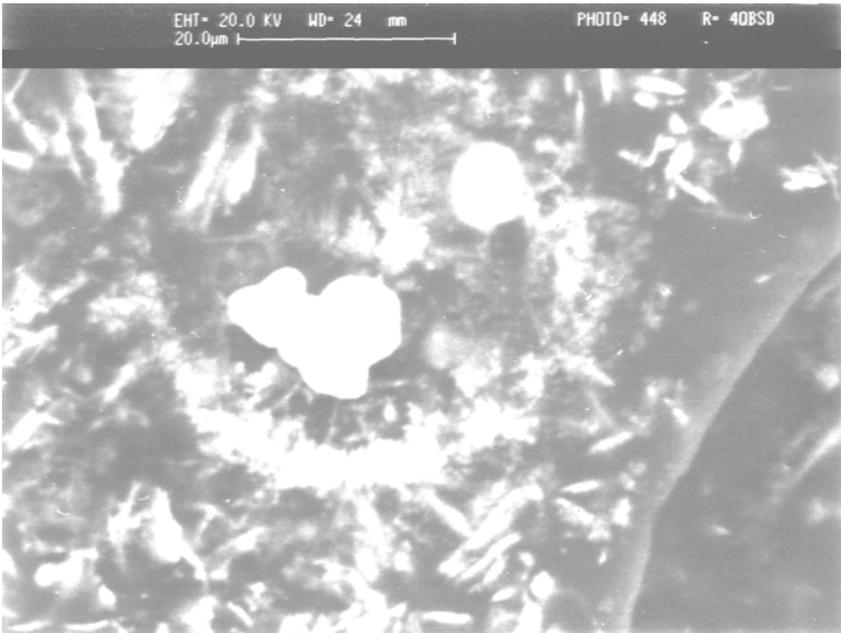
Radionuclides are an obviously unique feature of uranium mining wastes. Two radionuclides with contrasting half-lives provide good examples of the application of geochemical methods to hazard control.



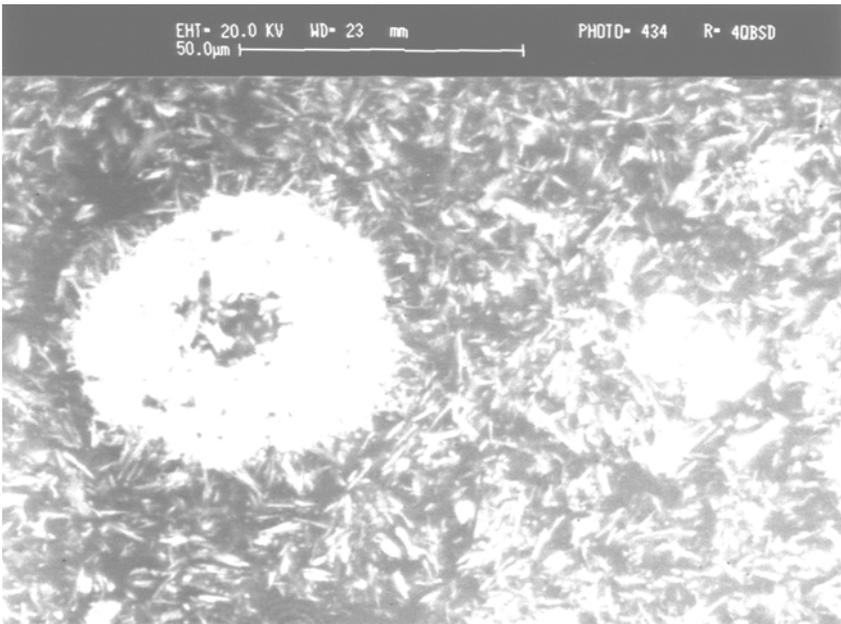
A: Fe-Mn oxyhydroxide rim containing trace amounts of U-Ti-Cu-Ni-As surrounding a gypsum-smectite core from neutralized raffinite. Cigar Lake, Canada



B: Fe-Mn oxyhydroxide – clay – quartz particle containing trace amounts of U-Ti-Cr in the oxyhydroxide bands. Process waste scale, Hem district, Czech republic



C: Arsenuranylite and boltwoodite in tailings. Rossing mine, Namibia.



D: Uranninite in waste rock within a matrix of gypsum from blended raffinite-waste rock. Cigar Lake, Canada.

Figure 9 Photomicrographs of Uranium mine waste

Radon-222 has a half-life of only 3.82 days, but it is hazardous because it occurs as a gas and can therefore be rapidly transported. The well established approach for controlling radon emanation from uranium tailings is to ensure that the tailings are covered with a layer of material, usually soil. The soil layer is sized so that radon transport through it is sufficiently delayed that the isotope never reaches the surface.

Radium-226 has a half-life of 1600 years, and occurs as an aqueous species. Radium-226 activities in tailings porewater at high grade operations can reach as high as 200 Bq/L. Barium chloride is added to tailings and raffinate solutions either prior to neutralization, immediately after neutralization, or as a separate effluent treatment step at most of the operating mines in Canada. The result is a co-precipitation of radium with barium sulfate. A series of surface and solid solution reactions result. Fundamental investigations by Beak Consultants (e.g. Constable and Snodgrass 1987) led to development of a predictive model that incorporated radium solid solution with barium sulfate, gypsum and anglesite. The model predicts that soluble radium concentration will decrease as tailings come into equilibrium with the initially supersaturated sulfate phases. This appears to be the case in the available field data.

5 CONCLUSIONS

It is the authors' collective experience that understanding the geochemical basis for contaminant behaviour is critical to the management of water quality at all mine sites. Operating and closed uranium mines represent an excellent example. The public attention and regulatory scrutiny given to the uranium mining industry has led to the development and application of many geochemical tools to understand, predict and manage water quality at uranium mines. This paper has presented several examples, many of which are applicable to other mining wastes.

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Metody prognozowania geochemicznego stosowane dla określenia jakości wód pochodzących ze składowisk uranu

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Streszczenie: Eksploatacja uranu niesie za sobą produkcję kilku geochemicznie złożonych odpadów. Złożoność ta wynika z różnorodności typów złóż, metod eksploatacji i obróbki rud oraz sposobów składowania odpadów. Celem określenia wpływu eksploatacji uranu na jakość wód stosuje się kilka metod prognozowania geochemicznego. Artykuł ten przedstawia kilka przykładów zastosowania takich metod, mających na celu określenie jakości wód, odsączających się ze składowisk z odpadami poeksploatacyjnymi uranu.