Geochemical modelling aids in mine closure – implications of orebody genesis to mine closure approaches

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Abstract

Safe and successful mine closure represents a fundamental work element that needs to accommodate the geochemical conditions existing at the completion of the mining and ore processing effort. Given the interests in limiting costs and time associated with mine closure efforts enhanced prior understanding of the geochemical conditions likely to exist upon exhaustion of the economic reserves can provide important benefits. The purpose of this paper is to document the benefits associated with geochemical modelling and understanding how the ore formation process may impact mine closure efforts, using one ore deposit type as an example. Specifically, this paper emphasises the geochemical processes leading to the formation of sandstone-hosted uranium roll-type deposits and how the resultant concentrations and distributions of ore and gangue phases need to be incorporated into understanding the geochemical conditions projected to exist at the end of mineral recovery efforts.

The paper describes the evolution of geochemical conditions leading to orebody formation and the geochemical effects induced by open pit mining and how these may be used to understand both the geochemical controls and constraints on residual mine water. In addition, a discussion will be provided on how these conditions may be simulated by solution equilibria and kinetic modelling to develop optimum approaches to achieve applicable closure standards. This paper also discusses specific augmentations to existing industry standard solution equilibria and kinetic models and associated thermodynamic databases to maximise the predictive accuracy of the geochemical modelling results. The benefits of understanding the electrochemically reactive behaviour of uranium and associated gangue phases and incorporating this behaviour into mine closure efforts are presented. The culmination of the benefits of the geochemical modelling will ultimately be the development of a sustainable approach to uranium mine closure that is based upon an engineered environment designed to return the orebody to stable geochemical conditions.

1 Geochemical processes leading to sandstone-hosted roll-type uranium orebody formation

Sandstone-hosted roll-type deposits represent an important uranium orebody-type especially within the United States (Adler, 1974). The geochemical processes postulated to lead to this type of orebody genesis was extensively studied beginning in the 1950s and extending up into the 1980s when the decline the price of uranium led to a general decline in associated economic and ore formation-related studies. The culmination of these decades of study, on the geochemical, sedimentological, stratigraphic, and detailed morphological processes thought to pertain to ore formation emphasised the critical role of oxidation/reduction reactions in the migration, precipitation, and continuous increase in solid phase uranium concentration resulting in an economically exploitable orebody (Hostetler and Garrels, 1962; Adler, 1974; Harshman, 1966, 1974; Granger and Warren, 1974; Langmuir, 1978). In summary, based upon the enhanced relative solubility of the uranyl ion (UO_2^{+2}), oxygenated groundwater carrying an elevated concentration of dissolved uranium, when encountering a pyritic/marcasitic geochemical reducing portion of the sandstone aquifer, results in the consumption of the dissolved oxygen and the associated reduction and precipitation of uranium. These precipitated low solubility uranous phases include both uraninite (UO_2) and coffinite ($USiO_4$) (Hostetler and Garrels, 1962; Langmuir, 1978). These studies also noted the importance of complexing agents, including carbonate and phosphate ions, in enhancing uranyl ion solubility.

The geochemically similar behaviour of selenium, vanadium, and molybdenum, whose oxyanions have comparatively elevated solubility relative to their geochemically reduced oxidation states, often results in

their co-association with uranium mineralisation (Harshman, 1966, 1974), either in direct proximity or laterally adjacent. The change in geochemical conditions from oxidising to reducing environments is manifested in an abrupt and visually dramatic change in coloration of the host sandstone. This colour change from red and yellow caused by the presence of ferric oxy/hydroxides within the oxidised portion of the aquifer; the "altered tongue", and the grey to black coloration of the pyrite/marcasite iron disulfide dominated reducing portion of the aquifer. The geochemically reduced portion of the aquifer hosts the economically viable concentrations of uranium and the majority of the co-associated gangue phases.

Often the uranium ore deposit is positioned below a low permeability shale or clay-enriched horizon preserving the mineralisation from surficial oxidation processes. Mining will remove this horizon allowing for the enhanced infiltration of oxygenated surface water contributing to the oxidation of any residual mineralised material. Although the economic mineral concentration of uranium is often present within the reduced sediments open pit mining constraints may require the excavation of some the adjacent oxidised tongue for logistical and safety reasons. This increase in the dimensions of the open pit mine may also help exploit any economic concentration of uranium within the "limbs" of the roll front that encompass the oxidised tongue. The implications of this action are discussed in the following section.

## 2 Geochemical effects induced by open pit mining

Most open pit mining operations try to employ a continuous backfill process, wherever possible. If no backfilling is included within the mine development processes the geochemical effects discussed below may be further enhanced by the influx of oxygenated surface water. The backfilling process usually requires that excavated material be placed within the same stratigraphic and elevation level from which it came. However, sub-economic oxidised and reduced materials tend to be intermixed within the former ore-bearing horizon. Additionally, in support of the mining operation, groundwater inflow is restrained by pumping or other physical means. The sub-economic material may have elevated selenium, vanadium, and molybdenum mineralised along with low concentrations of uranium. Pyrite and marcasite may also be included within the backfilled area. Removal of the ore-bearing sediment, with or without backfilling typically leaves a topographic valley or depression within the open pit outline. Upon cessation of mining and the restoration of unimpeded groundwater flow, well oxygenated surface water will tend to flow to this depression and readily penetrate vertically downward to re-establish the pre-mining hydrology and water table. This influx of oxidising water will react with the reduced mineral phases present within the backfilled material and/or with newly exposed reduced sediment present along the mine perimeter. As discussed by various authors (Hostetler and Garrels, 1962; Garrels and Christ, 1965; Langmuir, 1978) oxidisation of previously reduced mineral phases can result in enhanced solubility of uranium, vanadium, selenium, molybdenum and other metals and metalloids. Further, oxidisation of pyrite and marcasite can lead to a notable decrease in groundwater and exposed surface water pH. The geochemical effects of these reactions and their controls are discussed in the subsequent section.

3 Resulting geochemical controls and constraints on residual mine water

As discussed above, the primary geochemical reactions of concern relate to dissolved oxygen-based oxidation of reduced mineral phases. Consequently, an understanding of ground and surface water influx and the dissolved oxygen concentrations help provide insight into the type and impact of oxidation reactions. The constraint on oxygen supply will help limit both the rate and total mass of oxidation products generated. This is especially important in regards to oxidation of iron disulfide minerals present in the backfill and other newly exposed rock/sediments within and adjacent to the mine. Typically the pH of the ground and surface water, while depressed to a level below that of the pre-mining condition, is often constrained to a level above which, ferric iron-induced oxidation of sulphide and elemental sulphur within either pyrite or marcasite can engender the "propagation pyrite oxidation reaction":

$$FeS_2(s) + 14Fe^{+3} + 8H_2O \Rightarrow 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \qquad (1)$$

Rather, internal buffering within the backfilled material relative to the rate of iron disulfide oxidation constrains the acid generating reaction to the following:

$$2FeS_2 + 7O_2 + 2H_2O \Rightarrow 2Fe^{+2} + 4SO_4^{-2} + 4H^+ \qquad (2)$$
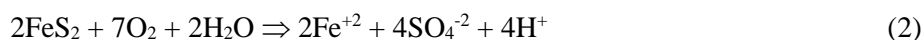
This finding (Granger and Warren, 1974) helps support the above assertion that oxidation reactions are controlled due to the influx of dissolved oxygen.

Although low pH may incrementally enhance the solubility of the elements of concern the role of oxidation to their high (and soluble) valance states is a far more important geochemical reaction. By modelling the rate of dissolved oxygen influx and subsequent kinetic and solution equilibria-based modelling, one can predict the progressive transformation and ultimate steady-state condition of groundwater in contact with the oxidising phases. Further, by estimating the mass and concentration of reduced phases one can estimate the total potential impact of the oxidising process and how these relate to environmental standards and the need for and benefits of mitigative measures.

Examples of the stoichiometry of the various oxidation-reduction geochemical reactions postulated to occur include the following:

$$2UO_2 + O_2 + 4H^+ \Rightarrow 2UO_2^{+2} + 2H_2O \tag{3}$$

Subsequent reaction between the uranyl ion and various complexing agents, such as dissolved carbonate, will engender the formation of relatively soluble uranyl carbonate complexes (Garrels and Christ, 1964; Langmuir, 1978).

Co-associated reduced phases will require additional oxygen to achieve their oxidation. Molybdenum disulfide, typically present as an amorphous "jordisite" phase [MoS_2] undergoes the following oxidation reaction:

$$2MoS_2 + 9O_2 + 6H_2O \Rightarrow 2MoO_4^{-2} + 4SO_4^{-2} + 12H^+ \tag{4}$$

It is notable that whereas uraninite [UO_2] only requires 32 grams of dissolved oxygen to result in the oxidation of 270 grams of mineral, jordisite [MoS_2] requires 288 grams of dissolved oxygen for the oxidative transformation of 320 grams of mineral. Further, pyrite and marcasite [FeS_2], which may be present in concentrations greater than either uraninite or jordisite, requires 224 grams of dissolved oxygen for the oxidation of 240 grams of mineral for the reduced sulphur species within these minerals. Consequently, it is vital to understand the overall oxygen demand of all quantitatively and reactive reduced mineral phases in order to assess the geochemical result of oxidative reactions.
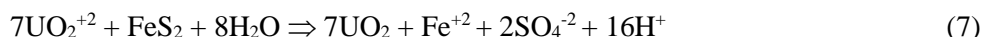
An example of a specific mitigative measure is to re-engender the initially reducing conditions that resulted in the attenuation and concentration of the economic and gangue phases. The application of biologically metabolisable organic substrates can simulate the biogenetically mediated sulphate reducing processes aiding in the consumption of dissolved oxygen and the reduction of dissolved elements of concern. Biogenic production of bicarbonate ion will also tend to help constrain a depressed solution pH via the following reaction, with CH_2O representing a simple carbohydrate:
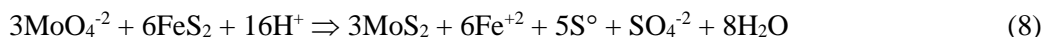
$$2CH_2O + SO_4^{-2} \Rightarrow H_2S + 2HCO_3^- \text{ (Berner, 1971)} \tag{5}$$

Similarly, subsequent re-reduction of these phases has different reductant demands.

$$4UO_2^{+2} + H_2S + 4H_2O \Rightarrow 4UO_2 + SO_4^{-2} + 10H^+ \tag{6}$$
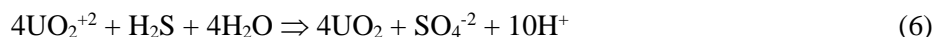
(1 unit mass of sulphur precipitates 29.7 unit masses of uranium).

$$7UO_2^{+2} + FeS_2 + 8H_2O \Rightarrow 7UO_2 + Fe^{+2} + 2SO_4^{-2} + 16H^+ \tag{7}$$

(1 unit mass of sulphur precipitates 26.0 unit masses of uranium).

$$3MoO_4^{-2} + 6FeS_2 + 16H^+ \Rightarrow 3MoS_2 + 6Fe^{+2} + 5S° + SO_4^{-2} + 8H_2O \tag{8}$$

(1 unit mass of sulphur will precipitate 0.75 unit masses of molybdenum).

Obviously, elevated concentrations of dissolved molybdate ion will have a correspondingly higher sulphide demand for different solutions having a fixed concentration of dissolved uranium.

Importantly, the numerous and geochemically inter-related reactions can be readily modelled via industry standards, solution equilibria and specially developed kinetic models. The kinetic models can be incorporated into certain solution equilibria models, such as the PHREEQC family of models (Parkhurst et al., 1980).

4   Augmentations to industry standard thermodynamic databases

Whereas many geochemical databases exist, it is important to confirm that all elements of concern are being modelled and that all important dissolved and solid phase constituents. Further it is necessary to ensure that the proposed solid phase compounds presumed to form are sufficiently kinetically reactive under ambient temperature and pressure conditions to readily form. Amorphous phases that are initially precipitated may be very much more soluble than a well crystalline, aged precipitate. It is important to ensure that the ionic strength of any modelled solution is consistent with limits defined by activity coefficients estimated within the program. The improper use of models can quickly result in an erroneous expectation of initial and long-term geochemical behaviour with potentially expensive consequences.

5   Benefits of geochemical modelling on mine closure

If properly employed the use of geochemical modelling can provide important cost and time-saving insights into mine closure-related matters. To more fully exploit this capability though it is vital to fully leverage geological and geochemical information collected as part of the overall mine development and evaluation process. All too often, the authors encounter concerned stakeholders who are challenged by an unexpected geochemical condition and are concerned that a costly and time consuming investigation will be required. By applying a *holistic, integrated, incremental* framework ("the *Hii* Road") ARCADIS geochemists have been able to provide important understanding to mining issues through the use of available geological and geochemical information collected, for example, for metallurgical testing, or ore genesis studies. It is through this understanding that a mitigation strategy integrated and consistent with the existing environment can be developed resulting in cost and time savings. Incompatibility with mine site environmental conditions can often cause a strategy to fail. If nothing else, geochemical modelling and the *Hii* Road Approach can pre-identify strategies that are incompatible with the present environment and are slated for failure.

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