

Uranium Sources and Mobility at an Iron Ore Mine Site in Northern Sweden

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Abstract

Discharge of process water containing uranium from an iron ore mine site in northern Sweden can be of environmental concern due to uranium's chemical toxicity and radioactivity. Water and solid samples were collected from the recipient and upstream along the mine value chain to identify potential sources of uranium and gain an understanding of the mobility of uranium. Mine water pumped from the open pit to the processing plant was identified to be the main source of uranium. $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and $\text{CaUO}_2(\text{CO}_3)_3$ -² dominated uranium speciation in the process water and promote uranium mobility from the mine site to the recipient.

Keywords: Uranium, Mine Water, Mobility, Sources, Recipient

Introduction

Potential contamination of recipients (natural lakes and rivers) by uranium (U) from mining is a global concern because dissolved U is linked to numerous health effects due to U's radioactivity and chemical toxicity. To prevent U contamination from mining operations, sources of U must be identified, and the mobility of U must be tracked along the whole mine value from mining, through processing and refining to the recipient where U is potentially causing harm. However, potential U sources can be difficult to identify at mine sites due to the multitude of water-rock interactions that occur between solid and liquid phases for example in the mine (underground or open pit), mineral processing plant, tailings dam, waste rock piles, thickening, and water treatment plants. In each of these steps, the chemical composition of the process water changes and determines the possible U aqueous species at the mine site.

Studies of U contamination in mining have been primarily conducted on specific steps of the mine value chain at U mine and mill sites, for example, on tailing dams, waste rock piles, and exposed mine workings. This makes it difficult to get a holistic view

of the mobility of U at the mine site in order to implement efficient prevention measures. Studies on the potential sources and release of U from iron ore mine sites where U can occur as a trace element but in concentrations exceeding the average crustal abundance are limited. Furthermore, U contamination studies that consider the critical factors that can affect U mobility along the whole value chain at a mine site are scarce. In this study, water and solid samples were collected at an iron ore mining site in northern Sweden to identify potential U sources and gain an understanding of the geochemical behavior and mobility of U.

Mine Site Description

The mine site is located in northern Sweden in the Kiruna Municipality. The ore deposit is an apatite-bearing iron ore deposit where magnetite is the main ore mineral and the main gangue minerals are apatite, calcite, actinolite, and quartz (Bergman *et al.*, 2001). The mine site consists of two open pits referred to as open pits A and B. Open pit A is currently mined at a rate of over 4 million tonnes per year whereas mining has ceased from open pit B. A mixture of infiltrating groundwater and precipitation

(referred to as mine water) is pumped from both open pits to be used in the processing plant where magnetite in the iron ore is concentrated. Grinding and wet magnetic separation are conducted alternately in several steps to produce a final magnetite concentrate, which is sent to pelletization. Slurry waste that consists of gangue minerals and magnetite that could not be recovered by wet magnetic separation in the processing plant is pumped to thickener 1 for water recovery. Water is recovered in an overflow product. The thickener 1 overflow is pumped to a return water tank, which is used to recycle process water back to the processing plant. A thickened slurry is recovered in the underflow of thickener 1 and pumped to thickener 2 where additional water is recovered in the overflow product and pumped to the storage dam. The underflow product is pumped to the tailings dam. The storage dam also receives water from the open pit B and acts as both a reservoir and a clarification dam where particles are allowed to settle before the process water is pumped back into the processing plant or discharged to the recipient.

Methods

Water samples (points 1 to 7) and solid samples (a to c) were collected in March 2021 to be able to identify potential U

sources (Figure 1) (Hegg, 2021). The samples were analyzed for their element concentrations by Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) at ALS Scandinavia AB in Luleå. Element concentrations in the solid samples were analyzed after lithium metaborate and $\text{HNO}_3/\text{HF}/\text{HCl}$ digestion. The pH, temperature, electrical conductivity (EC), anions (F^- , Cl^- , SO_4^{2-} , NO_3^-), cation (NH_4^+), and alkalinity (determined as HCO_3^-) were also measured in the water samples to determine the chemical conditions prevailing at the different water sample points. The element concentrations and chemical parameters at each water sample point were then used to calculate U speciation in PHREEQC Interactive 3.7.3.15968 (Parkhurst & Appelo, 2013) with the ThermoChimie thermodynamic database (Giffaut *et al.*, 2014).

The solid samples (samples a to c) were mineralogically characterized with Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) to identify U-bearing minerals. Sequential extraction tests focusing on the water-soluble (Milli-Q water), exchangeable (1M ammonium acetate, pH 7.0), and acid-soluble (1M sodium acetate, pH 5.0) fractions were conducted on the solid samples to distinguish mobile U, which can

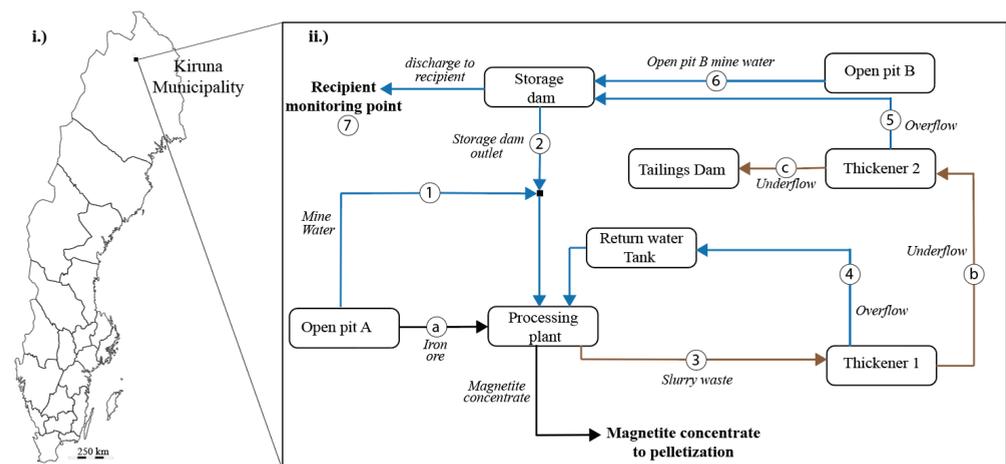


Figure 1 a) Location of the mine site in northern Sweden. b.) block flow diagram showing water (blue arrows), slurry (brown arrows), and solid (black arrows) exchange between the different components at the mine site. Water sample locations are numbered from 1 to 6 whereas solid sample locations are labeled from a to c.

be potentially released to the process water from stable U that requires weathering for U release to occur.

Results and Discussion

Chemical conditions and element concentrations

Water at the recipient monitoring point is characterized by close to neutral pH (7.4), low electrical conductivity (EC) (38.9 mS/m), and low element concentrations (Table 1). In contrast, process water at sample points 2 to 5 is characterized by alkaline pH of around 8.0, high EC, and high element concentrations. Temperature is highest at point 3 due to heat generation during grinding in the processing plant. The EC is higher at sample points 2 to 5, which are part of the process water recirculation system at the mine site compared to samples 1 (open pit A mine water), 6 (open pit B mine water), and 7 (monitoring point in the recipient), which are independent of the recirculation system. The higher EC at sample points 2 to 5 is due to the dissolution of soluble minerals such

as gypsum, halite, and sylvite and explosives containing NaNO_3 that are liberated during grinding and dissolve when they come into contact with process water in the processing plant (Karlsson *et al.*, 2017; Lundkvist, 1998). Process water recirculation at the mine site through the return water tank and storage dam also causes elements such as Ca, K, Mg, Na, Cl^- , SO_4^{2-} , NO_3^- , Sr, Ba, and Mo to accumulate in the process water over time and be higher in magnitude at sample points 2 to 5 compared to sample points 1, 6 and 7. Alkalinity was found to be the highest at point 1 compared to the other sample points. The U concentration is highest in the mine water from Open Pit A (59.9 $\mu\text{g/L}$) compared to the other sample points. Process water that is discharged from the storage dam has a U concentration above the maximum allowable limit of 8.6 $\mu\text{g/L}$ set by the Swedish Agency for Marine and Water Management in regulation HVMFS 2019:25. However, the U concentration at the monitoring point in the recipient (sample point 7) was 1.4 $\mu\text{g/L}$ due to dilution in the recipient.

Table 1 Chemical composition of the water sample points: 1) open pit A mine water, 2) storage dam outlet, 3) slurry waste from the processing plant, 4) overflow water from thickener 1, 5) overflow water from thickener 2, 6) open pit B mine water, 7) monitoring point in the recipient

Sample points	1	2	3	4	5	6	7
pH	8.2	7.9	8.3	8.2	8.1	8.1	7.4
Temperature (°C)	0.9	3.6	29.4	27.7	8	0	0
Conductivity (mS/m)	56.3	249	378	359	268	38.64	38.9
SO_4^{2-} (mg/L)	110	1100	1700	1600	1100	86	107.6
Cl (mg/L)	28	170	310	280	190	20	18.2
HCO_3^- (mg/L)	153	85	50	60	85	79	43
NO_3^- (mg/L)	0.58	9	16	14	9.7	0.17	0.86
Ca (mg/L)	78.9	428.0	639.0	607.0	461.0	52.9	49.8
K (mg/L)	7.1	55.9	88.70	103.0	62.7	4.4	6.1
Mg (mg/L)	12.8	36	55.1	54.3	39.4	6.8	5.4
Na (mg/L)	18.8	113	160	198	129	12.3	12.5
Sr ($\mu\text{g/L}$)	133	1170	1890	1920	1290	85.9	133.5
Ba ($\mu\text{g/L}$)	15.0	78.5	84.2	135.0	84.8	15.4	18.4
Mo ($\mu\text{g/L}$)	6.9	22.2	23.8	30.9	22.5	6.1	1.5
U ($\mu\text{g/L}$)	59.9	18	11.5	12.3	19.6	12.4	1.4

U speciation in the process water

U behavior is influenced by pH, Eh, U oxidation state (U^{4+} , U^{6+}), and the presence of common complexing ligands such as CO_3^{2-} , PO_4^{3-} , and SO_4^{2-} (Cumberland *et al.*, 2016). Through the weathering and oxidation of U(IV) minerals, U forms the more mobile and soluble U(VI) oxidation state, which occurs as the uranyl ion (UO_2^{2+}). Above pH 5 under oxidizing conditions, UO_2^{2+} forms carbonate complexes (CO_3^{2-}) of the form $UO_2(CO_3)_n^{2-2n}$, where $n = 1 - 3$ (Cumberland *et al.*, 2016). Depending on the availability of calcium (Ca), UO_2^{2+} can form the calcium uranyl carbonate complexes Ca ($UO_2(CO_3)_3^{2-}$) and $Ca_2UO_2(CO_3)_3^0$ above pH 7 (Bernhard *et al.*, 2001; Dong & Brooks, 2006. Geochemical modeling in PHREEQC suggested that the calcium uranyl carbonate complexes $Ca_2UO_2(CO_3)_3$ and $CaUO_2(CO_3)_3^{2-}$ dominate U speciation at all the sample points (1 to 7) (Table 2). The presence of calcium (Ca), and HCO_3^- in the process water and alkaline pH conditions prevalent at the mine site and the recipient are conducive to the formation of calcium uranyl carbonate complexes. Calcium uranyl carbonate complexes have been shown to enhance U mobility by reducing U's adsorption efficiency on mineral surfaces (Fox *et al.*, 2006).

U mineralogy and sequential extraction

U can occur as a trace element but in concentrations exceeding the average crustal abundance in iron ore. In the iron ore, U can occur in minerals of its own such as uraninite [UO_2], coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$], or pitchblende (UO_2), or in accessory minerals such as apatite [$Ca_5(PO_4)_3(OH,F,Cl)$], thorite [$(Th,U)SiO_4$], monazite [(Ce, La, Nd, Th) PO_4], or zircon [$ZrSiO_4$] (Misra, 2000). The U content in the iron ore (1.0 ppm) was lower than the average U content in the earth's crust (2.7 ppm) (Kalin *et al.*, 2005) (Table 3). Further downstream, the U content increased to 2.9 ppm and 3.2 ppm in thickener 1 (sample b) and thickener 2 (sample c) underflow solids, respectively. Further downstream, gangue minerals potentially containing U are concentrated as magnetite is recovered to the magnetite concentrate as indicated by the increasing Ca, Mg, Si, K, P, and Th concentrations compared to decreasing Fe contents in Table 3.

Sequential extraction was used to investigate the potential mobility of U and showed that more than 98 % of the U in the iron ore was associated with the residual fraction (Figure 2i). Further downstream at sample points b and c, more than 90 % of the U was associated with the residual fraction.

Table 2 Uranium speciation at water sample points 1 to 7

Sample location	1	2	3	4	5	6	7
$Ca_2UO_2(CO_3)_3$ (%)	89.83	97.06	97.56	97.78	97.56	86.83	80.62
$CaUO_2(CO_3)_3^{2-}$ (%)	9.64	2.86	2.38	2.12	2.38	12.59	15.74
$MgUO_2(CO_3)_3^{2-}$ (%)	0.50	0.08	0.06	0.05	0.06	0.51	0.56
$UO_2(CO_3)_3^{4-}$ (%)	0.03	0.00	0.00	0.00	0.00	0.06	0.19
$UO_2(CO_3)_2^{2-}$ (%)	0.00	0.00	0.00	0.00	0.00	0.01	1.14

Table 3 Element concentrations in solid samples; a) iron ore, b) thickener 1 underflow, c) thickener 2 underflow

Sample points	Fe (wt.%)	Ca (wt.%)	Mg (wt.%)	Si (wt.%)	K (wt.%)	P (wt.%)	Th (ppm)	U (ppm)
a	60.3	1.7	0.9	3.4	0.3	0.5	9.0	1.0
b	10.7	8.6	4.2	18.3	1.2	2.3	28.9	2.9
c	14.4	7.2	3.9	13.6	1.3	2.0	36.4	3.2

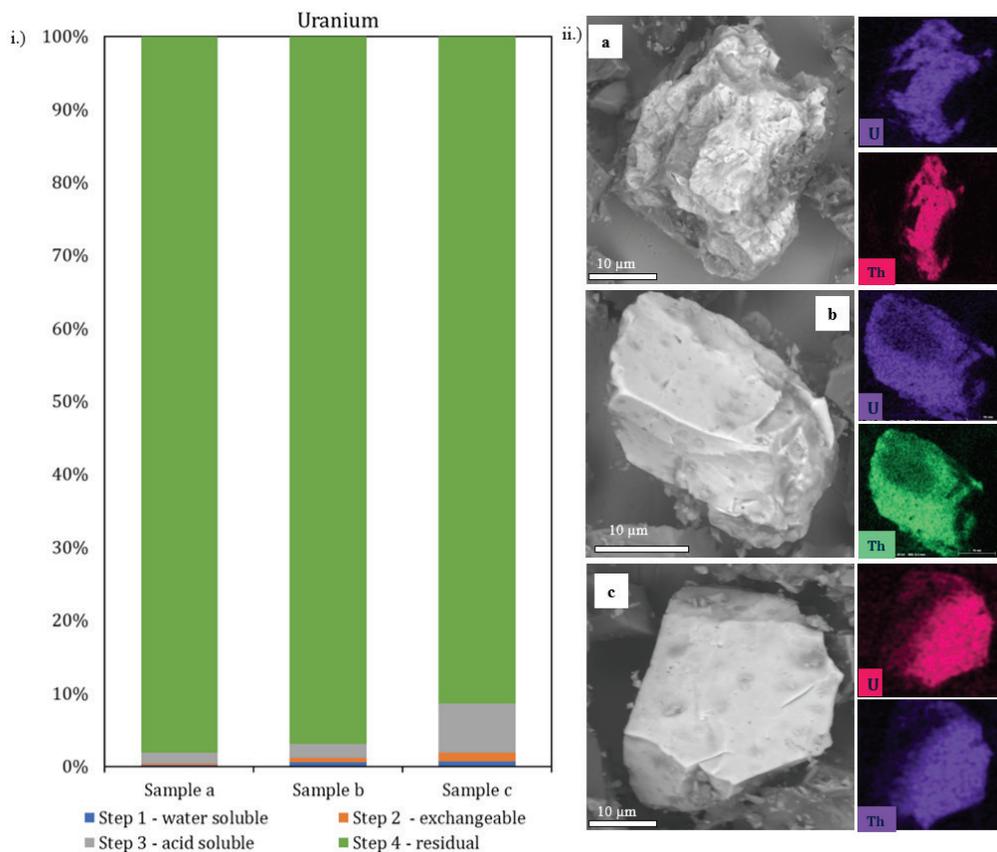


Figure 2 i.) Percent distribution of U in the iron ore (sample a), thickener 1 underflow (sample b), and thickener 2 underflow (sample c) solid samples. ii.) SEM images with U and Th distribution maps in samples a, b, and c.

In the residual fraction, U is strongly bound within mineral lattices and is not expected to be released to the process water. Mineralogical characterization by SEM-EDS revealed thorite containing 1 to 2 wt. % to be the main U-bearing mineral in the solid samples a to c Figure 2ii. Thorite is known for its low solubility and has been shown to dissolve mainly in aqua regia and hydrofluoric acid in thorium speciation studies (Guo *et al.*, 2007; Okeme *et al.*, 2022). Thorite insolubility at the different steps of the mine value chain is also supported by the fact that thorite grains identified downstream at sample points b and c looked unweathered and similar to grains identified in the iron ore (Figure 2ii). Therefore, the iron ore, which has a low U content where U predominantly occurs in the insoluble mineral thorite is not an important source of U to the process water.

Instead, the mine water that is pumped from the open pit to be used in the processing plant is a more important source of U.

Conclusions

- Mine water from Open pit A, which is a mixture of infiltrating groundwater and precipitation that is used in the processing plant is the main source of U to the process water. Further studies focusing on the open pit are required to identify U sources and gain an understanding of U-weathering processes that might be taking place in the open pit.
- The calcium uranyl carbonate complexes, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and $\text{CaUO}_2(\text{CO}_3)_3^{-2}$ were found to dominate U speciation at all the sample points. The presence of calcium (Ca), alkalinity (HCO_3^-) and alkaline pH

prevalent at the mine site are conducive to the formation of these complexes. The complexes enhance U mobility in the process water by stabilizing U in the process water and decreasing U's adsorption efficiency on mineral surfaces.

- Iron ore is not an important U source to the process water. The iron ore has a low U content (1.0 ppm). 98 % of U in the iron ore was found to be associated with the residual fraction which contains minerals where U is strongly bound in mineral lattices and is not expected to be released at the chemical conditions prevailing in the processing plant and thickeners.
- Thorite was identified as the main U-bearing mineral in the iron ore and thickener underflow solids. The thorite remains unweathered downstream in the thickener 1 and thickener 2 underflow solids indicating that it is stable along the mine value chain.
- The results highlight the importance of tracing contaminants upstream from the recipient along the mine value chain to identify potential contaminant sources.

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