Flood Water Treatment at the Former Uranium Mine Site Königstein – a Field Report

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Abstract

Due to the rather high uranium concentration of about 10 to 60 mg/l (maximum of 250 mg/l in 2002) in the acidic flood water from the former in-situ leach mine Königstein, a first treatment stage for uranium removal and processing has been implemented, followed by the further water treatment in a HDS (high density sludge) plant for neutralization and removal of various metals (Fe, Al, Zn, etc.), sulphate and naturally occurring radio-nuclides. In the late nineties, the former uranium plant was converted to a state-of-the-art processing unit meeting the specific requirements with regard to controlled flooding and recycling criteria for uranium.

Uranium processing includes ion exchange for uranium removal from the flood water, multi-stage elution, precipitation of uranium oxide (UOX), and UOX washing and de-watering for removal of dissolved impurities. HDS treatment efficiency and sludge de-watering properties were considerably improved by applying a staged neutralization technology to limit super-saturation of mineral phases as well as the formation of amorphous solids and to increase the precipitation rate of crystalline phases in significantly larger particles. Adsorption on Fe phases is important to remove various metals and radio-nuclides efficiently. Centrifuges are used for sludge de-watering to levels 48 M% solids (average), thus, enabling disposal of the de-watered sludge to a dump at the site directly.

This field report presents typical operational data and discharge water quality parameters meeting regulatory limits in all years of operation.

Key words: uranium, mining, flooding, remediation, ion exchange, uranium recycle, water treatment, high-density sludge (HDS), centrifuge, radionuclide, disposal

Introduction

The Königstein uranium mine (Schreyer and Zimmermann 1998) is exceptional because of the former combination of conventional mining (from 1971 to 1984) with in-situ leaching (ISL) applied from the early 80's to 1990. The geology consists of sedimentary strata (sandstone, chalk, and clay) with 3 ore horizons within the 4th aquifer consisting of Cretaceous sandstone overlaying granitic basement rocks. In-situ leaching (ISL) had been used in open mine works to recover uranium from ore blocks prepared with leachant inlet and leachate drainage systems (Jenk and Paul 2004). The sulphuric acid leaching led to a considerable contamination of the pore water, in particular with uranium, in a strongly acidic milieu. In order to avoid the wide-spread migration of contaminants into neighbored aquifer regions, flooding of the hydraulically isolated mine is performed in a controlled manner (Schreyer and Zimmermann 1998) including:

- Flood water catchment by a sophisticated drainage system via a control tunnel at the lower border line of the sloping mine aquifer,
- Pumping of the flood water to the surface and treating it in two process steps: uranium removal and water treatment (cf. Märten et al. 2002 and Heinze et al. 2002 for details),
- Automatic monitoring and process control (Märten et al. 1998).

Flood water hydraulics and chemistry

Flooding of the Königstein mine started from the base level at 25 mNN in 2001. In a first stage, a flood level at 106 mNN has been achieved until 2005, thus, increasing the total drainage to about 400 m³/h. After completion of additional preparatory works currently in progress the flooding will be continued step-wise in near-term, followed up in conjunction with a thorough monitoring program and model-based forecasts of flooding dynamics (Kalka et al 2002, Kalka et al. 2005) for decision-making purposes.

To demonstrate the main chemistry of the flood water, Fig. 1 represents the development of pH as well as uranium, sulphate and iron concentrations in the flood water from the beginning of flooding. In addition to these elements, there are considerable concentrations of heavy metals and natural radionuclides. The peak of uranium concentration observed in 2002 (about 250 mg/l) occurred due to post-leaching effects in high-grade ores close to the lower mine. Accordingly, there was a pH minimum (at 2.1) at the same time.

Figure 1 *Flood water chemistry at Königstein: pH, U, SO$_4$, and Fe concentrations in the main drainage flow*
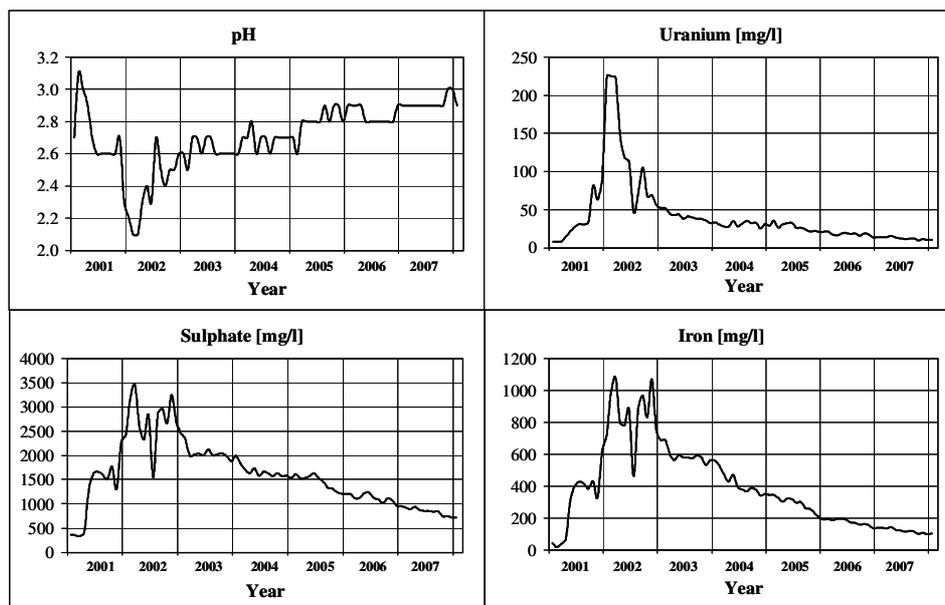
The flood water treatment plant with a capacity of 650 m^3/h has been designed to cope with the anticipated varying inflow conditions. The following section describes the technology (summary of more detailed papers (Märten et al. 2002, Heinze et al. 2002).

Technological overview

As schematically shown in Fig. 2, the flood water is treated in two main stages:
- Uranium removal (and further processing),
- Water treatment by the use of an improved HDS (high-density sludge) technology.

Uranium is removed from the flood water by anionic ion exchange. The resin load with uranyl sulphate species ($UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$) is mainly determined by the U concentration in the inflow and the (pH-dependent) relation to concentrations of competing anionic species like Cl^-, $Fe(SO_4)_2^-$, HSO_4^-, and SO_4^{2-}. Maximum U load on the resin (at given inflow composition) is achieved by applying counter-current sorption operation.

The considerable molar ratio of Fe over U in the flood water (in the order of 50:1) in conjunction with the high affinity of the resin with regard to U species (rather than Fe species) leads to a resin load ratio Fe:U of about 5:1. In order to suppress iron in the uranium processing to meet uranium oxide (UOX or Yellow Cake) product specification, resin elution and the subsequent precipitation stage had to be designed in a very specific manner as summarized below (cf. Märten et al. 2002 for more details).

The elution operation consists of the following stages (incl. Fe suppression):

[i]   Fe elution by a 0.1 M H$_2$SO$_4$ solution followed by a water flushing period (removing about 95 % of the iron)

[ii]   U elution by a 1 M NaCl eluant prepared from the recycled conversion eluate (step iii)

[iii] Resin conversion from chloride to sulphate form by a 0.1 M H$_2$SO$_4$ eluant, which is recycled afterwards to the eluant preparation for step (ii)

Uranium eluation works in a sequence of 3 columns (operated counter-current for maximum uranium grade in the pregnant eluate). Fe suppression in the first elution stage is efficient, however,

precipitation of the remaining small quantity of Fe in the pregnant eluate is still required to meet UOX specification. This Fe precipitation stage is operated as a cascade of 3 reaction tanks (controlled NaOH dosage to increase pH to 3.6, thus, eliminating Fe from the solution as ferric hydroxide).

The clarifier overflow is pumped to a reaction tank cascade with 4 reaction tanks to precipitate the uranium in continuous operation ($UO_2^{2+} + H_2O_2 + 2\ H_2O = UO_4 \cdot 2H_2O + 2\ H^+$). Hydrogen peroxide is added to the first 3 reaction tanks with a total stoichiometric excess of about 100 % in combination with a controlled NaOH dosage to achieve the optimum precipitation pH of about 3.5.

After thickening, the U concentrate is washed (for removal of dissolved impurities like Cl) and dewatered by operating a centrifuge in a sequence of 3 to 4 stages (with intermediate addition of pure water for diluting the liquid phase). As shown in Fig. 2, the Fe eluate from the first elution stage, the supermatant from uranium precipitation as well as the decant from the wash/de-watering unit are recycled to the flood water inflow.

Figure 2 *Technological scheme of the flood water treatment plant at Königstein*
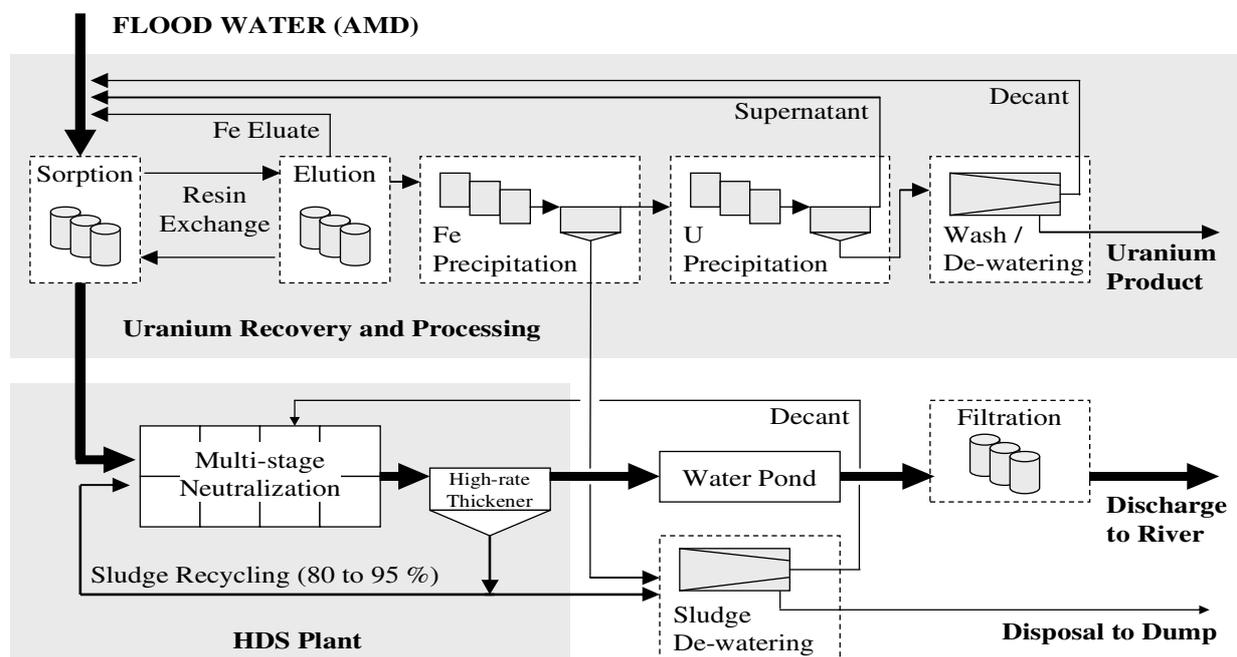
HDS technology is a standard for treating acid mine drainage (AMD). It includes neutralization (by lime dosage), flocculation and sedimentation, combined with both oxidation (depending on inflow chemistry) and partial recycle of the thickener underflow to the neutralization inflow. In the present application case, the conventional HDS technology had been improved by implementing staged neutralization as tested in laboratory scale with NaOH by Demopoulos et al. (1995). It is the main advantage of staged neutralization that supersaturation of relevant phases in the neutralized suspension is limited, thus, suppressing the precipitation of amorphous ferric phases (hydroxides) and favouring the precipitation of crystalline solid phases like basic ferric sulphate $FeOHSO_4$ or more complex mixed phases like Schwertmannite $Fe_8O_8(OH)_6SO_4$ (or similar formulae), in addition to gypsum precipitation, if applicable. The Königstein HDS plant consists of a

- Two lime neutralization lanes with 4 reaction chambers each, all aerated for agitation and complete oxidation of ferrous to ferric iron, in combination with a
- High-rate thickener (improved separation by feed inlet into the pulp bed).
  HDS based on staged neutralization together with high-rate thickening is advantageous with regard to
- Increased settling rates (larger and more compact solid particles)
- Increased sludge density in the underflow of the thickener

    – Improved sludge de-watering properties, even enabling the use of centrifuges to de-water the sludge to 48 % solids (average) in routine operation, thus, producing compact and stable solids suitable for direct disposal on the dump at the site (without further conditioning).

Due to the considerable iron concentration, heavy metals and radionuclides are efficiently removed by adsorptive effects mainly (so-called co-precipitation). Finally, the cleaned water passes a holding pond and (for absolute safety) a filtration unit before discharging to the Elbe river.

Performance

From the very beginning, the Königstein plant has always met regulatory and economic requirements with regard to

    – Water discharge parameters (see Table 1 for 2007 data),
    – UOX quality (for sale),
    – Sludge parameters (both geophysical and geochemical) for safe disposal.

Table 1 *Flood water and cleaned water data in 2007 (averages) with reference to regulatory limits*

	pH	Fe [mg/l]	U_{total} [mg/l]	Al [mg/l]	Mn [mg/l]	^{226}Ra [mBq/l]
Flood water	2.6	112	13.7	21.9	6.0	8,980
Discharge limit	6.5-8.5	2.9	0.5	2.0	3.0	800
Discharge data	7.3	0.2	0.02	0.3	1.4	35

Note that the U concentration in the flood water is reduced to 0.59 mg/l (average in 2007) after IX sorption. Most of the remaining dissolved uranium is precipitated in the HDS plant.

As demonstrated by Heinze et al. (2002), all relevant metals like Ni, Cr, Zn, Pb, As, Cd and Cu are removed from the flood water down to levels < 0.02 mg/l in the treated water. The (chemically) more critical Mn is reduced to 1.4 mg/l by adsorption on iron phases at neutral pH (cf. details and model results in Heinze et al. 2002). The technology implemented at Königstein is well proven, in particular after coping with the most critical conditions in 2002 (cf. Fig. 1). The stable long-term operation of the whole plant is supported by regular maintenance.

The next stage of mine flooding (from the current level at 106 mNN) will be initiated in near term, hence, leading to an increase of pollutant concentrations in the flood water again. Further flooding will be performed in a strictly controlled manner to keep underground pollutant migration in tolerable limits and to avoid/minimize contamination of aquifer systems around the mine.

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