Passive Barriers for Long-Term Containment of Uranium and Vanadium

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Abstract Mine closure plans require long term and stable strategies for containment of mined and associated metals and other pollutants. For several mining projects in the semi-arid Erongo Uranium Province, Namibia, an approach has been developed that combines containment and immobilization strategies based on geochemical processes. The approach is based on understanding and reconstructing *in situ* and geochemical conditions and processes that favored the enrichment and trapping of mined and associated substances. Hydraulic conditions that originally favored entrapment are included. Laboratory experiments on most suitable local material for passive barriers (sand, gypsum, crushed carbonate and iron hydroxides) as an environmental safety barrier were evaluated.

Keywords Mine closure, passive barriers, Uranium, Vanadium

Introduction

Concepts for passive barriers based on natural material for uranium and vanadium retention have been investigated within the framework of mine closure plans for carnotite-based mining operations (Dahlkamp 1993) in the Erongo Province of Namibia. The study area is characterized by semi-arid to arid climate with rainfall ranging from 150 to 100 mm per year and scarce flood events. Groundwater recharge in the study area is about 1–3 % of rainfall or 1–4 mm m^{-2} per year. Therefore groundwater flow is small and concentrates in shallow alluvial aquifers. The basement complex of the Erongo Region that is composed of granite, orthogneiss, amphibolite and schist is characterized by complex groundwater flow system with low fluxes and lithological and structural control. The low fracture volume, however, induces high groundwater levels in basement rock compared to porous aquifers resulting in subsurface discharge into alluvial aquifers that host the carnotite deposits. A mine closure plan and containment concept was developed taking into account these regional conditions of the Erongo Uranium Province.

Methods

The concept is based on several principles: Groundwater movement in alluvial aquifers is orders of magnitudes faster than groundwater movement in adjacent bedrock. Alluvial aquifers are subsurface drainage tubes for draining surrounding basement aquifers. Paleochannels are overlain by calcrete on which active sandy channels are episodically flooded. Hence, there is a system of four flow velocities: groundwater flow in bedrock (10^{-9} to 10^{-7} m/s), groundwater flow in buried paleochannels (10^{-8} to 10^{-7} m/s) and in recent alluvial aquifers (10^{-6} to 10^{-5} m/s) as well as episodic floods in ephemeral channels (10^{0} to 10^{-1} m/s). In the paleochannel and in the active channel transport velocity is further controlled by species-specific adsorption-desorption, precipitation and phase equilibrium reactions at the rock-water interface. For surface flow such controls are not effective. At all means a resurgence of polluted groundwater, subsequent evaporation and deposition of dissolved uranium or vanadium at channel surface of dry riverbeds need to be avoided as this would lead to a rapid transport of uranium and vanadium

downstream by surface flow. The fact that uranium and vanadium concentrations in river sediments and channel groundwater downstream are very low (10–25 µg/L) indicates that there has been a natural mechanism of containment in place before mining and that these species have not entered surface flow transport path so far.

Groundwater flow in the basement aquifer is low but cannot be neglected in a long-term mine-closure and containment concept. All evidence from hydrochemical data, ^{14}C dating, tritium measurements, CFC residence time analysis and hydrochemical evolution along transects, as well as water level readings suggests that groundwater flow from the basement towards the alluvial aquifer system can be taken as a general feature of the region.

A first hydraulic principle of containment concepts for Uranium in the Erongo Uranium Province is the convergence of basement flow towards alluvial aquifers. A containment con-

cept in this region therefore needs to assure that groundwater does not re-surface to avoid that evaporative crust or precipitates can be taken away by surface flow. Plumes need to be contained within the previously existing and Uranium-bearing paleochannels aquifers. This pre-condition can be achieved if hydraulic capacity of the reconstructed paleochannel (Fig. 1, L3) is sufficiently large to discharge groundwater recharge of the entire upstream catchment.

The dashed area contains carnotite and is mined. This part of the channel can be refilled with dried tailings material and waste rock. It is proposed to use waste rock as a scour protection on top of tailings material to prevent vertical erosion of the active alluvial channel. An important feature of the hydraulic concept is to maintain the lower part of the paleo-channel (L3) as a subsurface drainage for groundwater discharge from the upstream catchment. Re-filling this section with low-permeable ma-
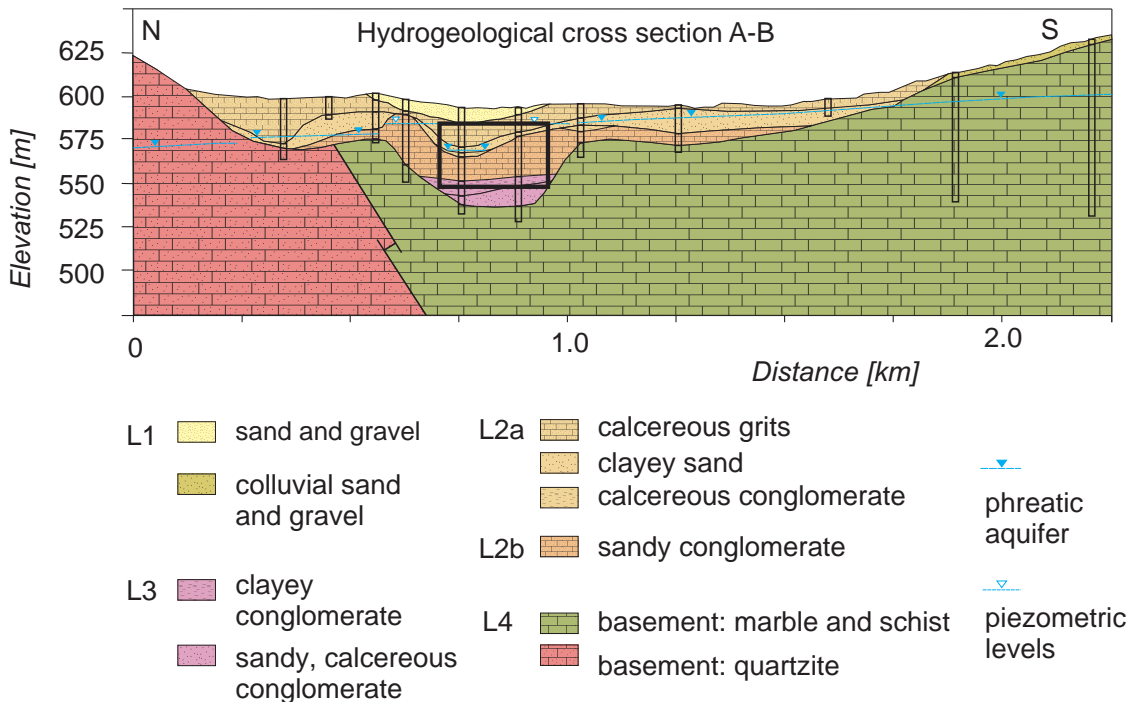

Fig. 1 *Schematic cross-section of a paleo-channel L2, L3 and ephemeral channel L1 containing a sequence of clayey conglomerate (L3) and carnotite bearing calcrete and calcereous grit, the dashed area is mined and refilled with tailings and waste rock (scouring)*
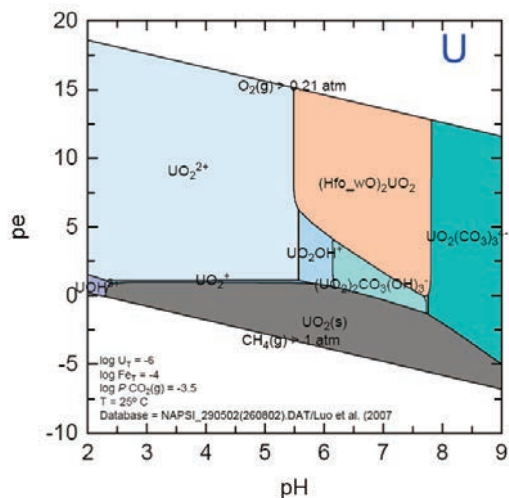
Fig. 2 *Mobility of uranium in a pH-pe diagram including surface complexation processes (Hfo_wO)$_2$UO$_2$. Mobility is constrained by solid UO$_2$ (grey) and by surface complexation on iron-hydroxide coatings or other complexing surfaces (beige/orange). Calculations are based on PhreeqC (Thortenson and Parkhurst 2002) and PhreePlot(Kinniburgh and Cooper 2011)*

terial could lead to a rise of groundwater level and connection with the active ephemeral channel. As tailings material is sufficiently fine it acts as a confining layer. Such a refilling sequence re-establishes the original hydraulic system that is knows to have provided hydrogeological conditions that contained uranium and vanadium before. The efficiency of these processes in trapping uranium and vanadium is such that downstream of shallow carnotite deposits of the Erongo Uranium Province uranium and vanadium concentrations in the alluvial aquifer and shallow groundwater are often below 10–25 µg/L.

A second key principle in long-term mine-closure and containment concept for this type of mine is to re-establish geochemical conditions that immobilize uranium and vanadium for good. Equilibrium thermodynamics of carnotite and of uranium and vanadium species in saline to fresh groundwater of carbonate rock have been analyzed and modeled (Pirlo *et al.* 1984; Pirlo and Giblin 2004). The occurrence of species and solubility of uranium and vanadium depends on pH, redox conditions and the activity of other complexing species in groundwater (Langford 1974). Uranium tends to form mobile species at pH < 5.5 and at pH > 8.5-9.0 and at positive pe values, mobility decreases in neutral and reducing conditions. Mobility of Vanadium increases

with increasing pH and with the increasing activity of negatively charged Vanadium (V) species. In addition to pH and redox conditions, salinity, alkalinity and the presence of complexing agents affects transport and mobility (Mann and Deutscher 1978).

The second key principle of the mine closure and containment concept is to use thermodynamic controls on uranium and vanadium mobility and to try and keep ambient conditions around the re-filled tailings material and waste rock within a range that provides low mobility. All blue species have a certain degree of mobility: While mobility in the acidic (pH < 5.5) and basic domain(pH > 8.0) is given at pe ≈ 0, there is only a narrow bridge of mobility for pe-conditions near 0: at lower pe precipitation occurs and solid immobile UO$_2$ (s) is the prevailing thermodynamically stable species, at higher pe surface complexation imposes limits on uranium mobility, provided reactant surfaces for surface complexation such as iron hydroxides are available (Fig. 2).

The mobility of uranium and vanadium for typical groundwater chemistry in the Erongo Uranium province ranging from saline groundwater in basement rock to fresh groundwater stemming from flood recharge was investigated and modeled using PhreeqC (Thortenson and Parkhurst 2002) and Phree-
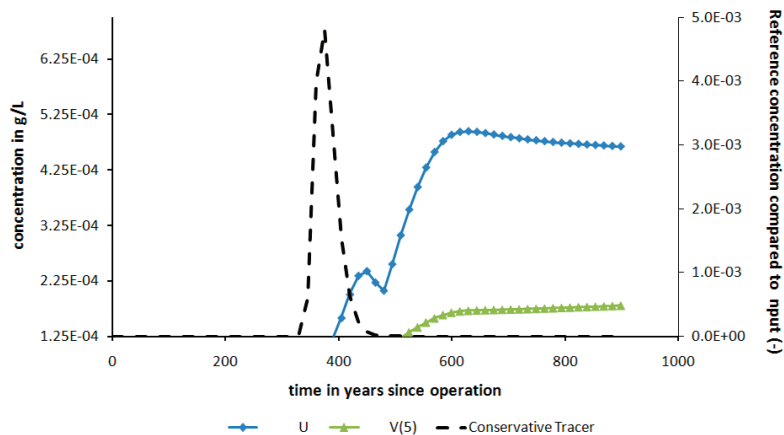
Fig. 3 *Modeled transport of a reference tracer (pulse of chloride at mine closure) and of uranium and vanadium released from tailings material*

Plot (Kinniburgh and Cooper 2011) at several sites. Thermodynamic calculations have been combined and coupled with advection dispersion transport for given and measured hydrochemical composition to account for species-specific transport stable species. Results of such calculations are given in Fig. 3. The transport of a pulse of conservative species (chloride) was always given as reference. However, the conservative tracer also fully accounts for dispersion effects during advective and dispersive transport. Retention and retardation of uranium and vanadium was found to depend on water chemistry (salinity, alkalinity, and pH) of other groundwater components from basement rock and on the composition of tailings (water content, alkalinity). A significant dispersion and retardation of uranium and vanadium was found.

Coupled reactive transport can be modeled for a range of initial conditions for a given groundwater chemistry and for a range of aquifer characteristics (hydraulic conductivity, porosity, geochemical composition of aquifer material). Sorption on exchange sites and surface complexation on iron hydroxide coatings were included. The surface of exchange sites and of surface complexants was determined from samples taken potential sites.

Finally, passive barriers were investigated as a third mechanism for containing uranium and vanadium within the mined area after mine closure. In the regional context of the Erongo Uranium Province, paleochannels and alluvial channels play a key role for retention. Due to the hydrogeological setting found, groundwater flow naturally converges in paleochannels and alluvial channels. Passive barriers in these channels can therefore be used as a third retention mechanism. If uranium and vanadium transport takes place passive barriers can retain these species. For economic reasons only materials available directly within the vicinity of the mine were investigated that can be transported easily and that just need to be separated mechanically on the site. Quartz sand, iron coated sediments (clays, mixed with sand), crushed gypsum and carbonate (not carnotite bearing) were investigated. Their retention capacity was tested using column experiments in the laboratory. To assure conditions similar to those found in the study area, transport calculations were carried out a) using a hydrochemical composition similar to that found in the study area (synthetic water hydrochemistry corresponding to major ion composition, electric conductivity, pH and alkalinity). Complexing agents such as fluoride and phosphate were not considered, they are also not relevant in the study area. Uranium and vanadium concentrations resembling to those found in the study area or expected in tailings materials were used. Experiments were carried out for several months, running several batches with 500 and 50 µg/L of uranium and vanadium.

Results

Results indicated that also natural materials such as quartz sand and iron hydroxide coated clays have a significant retention potential. Gypsum was found to have a specific retention capacity for vanadium but not for uranium. Carbonate was found to have the lowest retention capacity. The sorption capacity of quartz sand was found to be higher than that of iron hydroxide. As the desorption coefficient of iron hydroxide was by far the lowest the best material to be used in passive barriers is iron hydroxide coated clay mixed with quartz sand. Carbonate and gypsum, however play an indirect role in controlling transport by affecting pH and alkalinity as well as overall salinity of groundwater.

Conclusions

A mine closure and retention concept for the Erongo Uranium Province was investigated. The focus was on shallow carnotite-type associated uranium deposits associated with calcrete crusts and found in and on top of paleochannels, partially covered with ephemeral channels. A concept based on three mechanisms is proposed: Reconstruction of the hydraulic system, investigation of geochemical retention processes and modeling and finally a passive barrier system using natural materials as a backup. Functioning of passive barrier systems was investigated in the laboratory and found to be a safety option for uranium and vanadium retention.

References

Dahlkamp FJ (1993). Uranium ore deposits. Springer Verlag.

Giblin AM, Batts BD, Swaine DJ (1981). Laboratory simulation studies of uranium mobility in natural waters. Geochimica et Cosmochimica Acta, 45(5), 699–709.

Kinniburgh D, Cooper D (2011) PhreePlot. Center for Ecology & Hydrology, UK., 584 p.

Langford FF (1974). A supergene origin for vein-type uranium ores in the light of the Western Australian calcrete-carnotite deposits. Economic Geology, 69(4), 516–526.

Mann AW, Deutscher RL (1978). Genesis principles for the precipitation of carnotite in calcrete drainages in Western Australia. Economic Geology, 73(8), 1724–1737.

Pirlo MC, Giblin AM (2004). Application of groundwater–mineral equilibrium calculations to geochemical exploration for sediment-hosted uranium: observations from the Frome Embayment, South Australia. Geochemistry: Exploration, environment, analysis, 4(2), 113–127.

Thortenson, Parkhurst (2002) Calculation of individual isotope equilibrium constants for implementation in geochemical models. Water-Resources Investigations Report 2002–4172