Determination and modelling of geochemical speciation of uranium in gold mine polluted land in South Africa

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ABSTRACT

The East and Central Rand of the Witwatersrand has been one of the most important gold mining areas in the world. One of the environmental consequences of this mining activity has been the release and distribution of heavy metals into the ground and surface water systems as a result of acid mine drainage arising from oxidation of pyrite (FeS_2) in the tailings dumps.

The research is aimed at the quantitative assessment of the distribution of uranium and the modelling of its geochemical speciation in gold mine polluted land.

Uranium in the form of uraninite (UO_2) and brannerite (UTi_2O_6) is normally associated with gold-bearing ores and studies of samples collected from the study area revealed high concentrations.

Analyses of dump material indicate that U is being selectively separated from its decay products in the dumps, resulting in locally high concentrations of U. It is possible that such areas of enrichment may not be detectable by conventional gamma ray spectroscopy because of separation of U from its decay products. Separation occurs as U is oxidized to the U (VI) state. Chemical modelling indicates that U occurs predominantly as uranyl-sulphate complexes in the water, which are soluble over a wide pH range. Neutralization of the acidic water in swamp environments is associated with removal of U. This is partly due to adsorption or co-precipitation on Fe and Mn oxides, and partly due to reduction of U to the U (IV) state.

1. INTRODUCTION

The metropolis of Johannesburg, South Africa’s largest city and financial centre, owes its origin to the gold-bearing conglomerates of the Witwatersrand Basin. This basin consists of a vast accumulation of ancient sedimentary rocks, including the gold-bearing conglomerates in the upper part of the rock sequence known as the Witwatersrand Supergroup. These are believed to have been deposited about 2800 million years ago in a fluvial and shallow marine environment by rivers that flowed into the basin. The Witwatersrand Basin is roughly oval in shape, approximately 350km in a north east to south west direction and stretching over 150km across (Fig. 1). Most of the mining activity in the East and Central Rand occurred between 1886 and the early 1970s, with total gold production reaching over 18000 tons (almost half of the gold ever mined in the world comes from the Witwatersrand Basin) [1].

The gold-bearing conglomerate mined in the Witwatersrand area has a typical mineralogical composition of [2]:

- Quartz (70-90%);
- Phyllosilicates (10-30%), consisting mainly of sericite, $KAl_2(AlSi_3O_{10})(OH)_2$;
- Accessory or minor minerals (1-5%) such as uraninite (UO_2), monazite, chromite ($FeCr_2O_4$), pyrite (FeS_2) and rutile (TiO_2).

More than 70 minor minerals have been identified in the reefs, the most abundant being pyrite (FeS_2) with an abundance of 3-5%. Uranium is present in the form of uraninite (UO_2) or brannerite (UTi_2O_6) and is associated with galena (PbS) in the Witwatersrand-type auriferous ores. In some regions of the basin, uranium concentrations were sufficiently high to make economic extraction possible.

Mining operations in this region have left a legacy of pollution in the form of acid mine drainage emanating from tailings dumps. Residual sulphide minerals, especially pyrite, in these tailings dumps are unstable when exposed to atmospheric oxygen and undergo oxidation resulting in the generation of acidity and the release of heavy metals and metalloids. The oxidation of pyrite can be described by the reaction:

$$FeS_{2(s)} + 7/2O_2 + H_2O \rightarrow 2SO_4^{2-} + Fe^{2+} + 2H^+$$

Similar reactions involving other sulphide minerals can release dissolved As, Cu, Cr, Ni, Pb, Co and Zn. The products of this reaction are often transported downwards by percolating rain water into the underlying aquifers. Neutralising reactions, with mineral phases in sediment, often consume the acidity resulting in a groundwater plume at near-neutral pH but containing high concentrations of Fe and SO_4^{2-}. Upon discharge to nearby surface water bodies, ferrous iron undergoes oxidation and precipitates as ferric oxyhydroxide mineral phases:

$$Fe^{2+} + 1/4O_2 + 5/2H_2O \rightarrow Fe(OH)_{3(s)} + 2H^+$$

This reaction is also acid generating and the resulting low pH conditions can greatly increase the mobility and toxicity of dissolved heavy metals. In many cases, the flux of the acid drainage from tailings impoundments will continue for many decades [3].

In this paper, the results of the distribution and speciation of uranium as a result of acid mine drainage are reported.

2. PREVIOUS INVESTIGATIONS

Numerous studies have been carried out to assess the pollution caused by previous mining operations on the Witwatersrand. A study [2] was carried out to show that even decades after decommissioning of mining operations, significant loads of salts, heavy metals and in some cases radionuclides remain beneath reclaimed tailings dumps.

Another study [4] revealed that acidified water seeping from the mine tailings dumps contributes an average of about 20% of stream flow of the Natalspruit in the Witwatersrand watershed. This reduces pH, adds high metal loads to the water and causes extreme iron hydroxide precipitation in the stream, all of which impact negatively on aquatic life.

One study [5] reported the results of an investigation into the condition of the soil exposed after reclamation of slimes dumps to the east of Johannesburg. Their results revealed elevated concentrations of heavy metals in the topsoil. They predicted that while most of those metals were not labile forms, they would in the long run be leached into the ground water.

Most of the studies which have been conducted previously focus mainly on a generalized view of pollution by heavy metals. Few of them have been directed at studying radioactive trends, particularly the speciation and distribution of uranium.

Another study [6] revealed that there were elevated concentrations of cyanide and trace metals such as Cd, Co, Cu, Fe, Ni, Mn, Pb, Ra, U and Zn in seepage samples from gold mines. Very low concentrations of U were found in samples which were collected from the seepage plumes down gradient and down wind of tailings. However, significant radiometric anomalies were detected during airborne radiometric mapping surveys over mining areas. The radiometric studies [7, 8, 9] revealed that high gamma-activities emanating from immobile daughters such as ^{226}Ra of the U decay series in tailings dams pose a serious threat to the nearby environment as a result of dust dispersion.

3. THE STUDY AREA

Geologically, the East and Central Rand have been well documented [10]. They contain six major auriferous conglomerate layers, two of which have been extensively mined (Main Reef Leader and South Reef), three patchily mined (Main, Bird and Kimberley Reefs) with one low grade reef (Elsburg) largely unmined.

The climate is temperate, highveld, with a short cold winter and a hot summer. The rainfall occurs predominantly in summer. Annual precipitation ranges from 600 to 732mm. During the period from October to March, the area often experiences heavy storms. The average annual temperature is about 16^{o}C [11].

The area (Fig. 2 and 3) is characterized by a well defined drainage system including streams, dams and wetlands which form the tributaries of the upper Klip River. The streams include the Klipspruit, Natalspruit and Russel streams, while dams and wetlands include New Canada Dam, Wemmer Pan and Rosherville Dam. The Klipspruit flows southwards and drains the Consolidated Main Reef (CMR) mining area and the western side of Crown Mines (CM) while on the City Deep (CD) side, to the east, the streams converge into the Natalspruit. Further east of City Deep (East Rand) streams converge into the Elsburgspruit. Dams on this side include Boksburg Dam, Victoria Lake, Cleveland Dam, Elsburg Dam and Angelo Pan. The stream patterns in the study area are of importance since they drain the reef outcrop, areas of tailings dumps and old mine workings which serve as a source of pollution to both surface and ground water.

4. MATERIALS AND METHODS

4.1. SAMPLING PROCEDURES

Water samples were collected at the beginning and end of the wet season (September and May respectively) in 2002. These were collected from the middle of the streams for surface water while ground water samples were collected from auger holes by the stream banks after allowing for equilibration. The water samples were collected in clean, acidified polypropylene bottles, filtered in the laboratory and refrigerated at about 4^{o}C [12]. Sediments were collected at about 20cm depth intervals from auger holes. The sediments were sampled at the Rosherville dam wetland. Tailings dump material was collected at random, mainly to assess radioactive disequilibria. The solid samples were stored in PVC bags with sediments being refrigerated while tailings dump material was stored in a cool, dry and dark place.

4.2. FIELD MEASUREMENTS

The measurement of the geochemical parameters: conductivity, dissolved oxygen, pH, redox potential, and temperature were taken for each water sample during sample collection using standard procedures employing field meters [13]. The above characteristics of water which are important for modeling of speciation are impossible to preserve in a collected sample and so must be measured in the field.

4.3. ANALYTICAL METHODS

Field measurements were recorded using a Universal Multiline P4-SET3 field meter (WTW, Germany) equipped with pH combined electrode with integrated temperature probe (SenTix 41), standard conductivity cell (Tetra Con 375) and oxidation-reduction potential probe (SenTix ORP). The pH electrode is calibrated according to IUPAC recommendations against two buffer solutions at pH 4 and pH 7. Redox potentials are obtained from Pt electrodes versus Ag/AgCl. The electrodes are checked by a standard buffer solution. All potentials reported are corrected relative to the standard hydrogen electrode (SHE).

There is no accepted method to estimate an uncertainty of a field pH determination. The applied two point pH calibration, recommended by IUPAC, does not allow an estimation of an uncertainty directly from the calibration line [14, 15]. Therefore, an uncertainty of about ± 0.1 pH units (1σ) is supposed. Redox potentials are affected by the weak mineralization of most natural waters, poisoning of Pt electrode surface or the influence of several redox systems [16]. As a summary parameter, Eh constitutes an important parameter characterizing a natural water system. An uncertainty of ± 30mV is assumed that corresponds to the average fluctuation observed during field sampling.

Tailings dump samples were air dried and then sieved to a size <2mm. Samples to be analysed by gamma ray spectroscopy were weighed (mass of about 500g) then filled into Marinelli beakers. The samples were stored for about two weeks to reach the corresponding radioactive equilibrium.

A γ-spectrometer (ORTEC) was used for analysis whose main component is an n-type high purity Ge detector with 36% relative efficiency and 1.8keV line width at 1.3 MeV. It is surrounded by a passive shielding of 9 cm lead, 2 cm mercury and about 0.5 cm electrolyte copper. The spectra were analysed by comparing the net peak count rates (counting time was 2 hours) with the count rates of a calibration source of the same measuring geometry. The effect of self absorption was taken into account during the activity determination. For the ^{238}U series, ^{226}Ra, ^{214}Pb and ^{214}Bi were analysed while for the ^{232}Th series, ^{228}Ac, ^{212}Pb and ^{208}Tl were analysed. ^{214}Bi (at 609.3keV) and ^{228}Ac (at 911.2keV) were used as proxies for the ^{238}U and ^{232}Th series respectively because of their strong ability to emit γ-radiation. Radioactive standards containing 0.527% U_3O_8 and 0.4% ThO_2 were used to obtain calibration curves. The standards were supplied by the International Atomic Energy Agency.

The concentrations of metals in samples were determined using a Spectro Ciros Inductively Coupled Plasma Optical Emission Spectroscope (ICP OES) with a coupled charge detection system (CCD). Calibration was carried out using certified standards (Industrial Analytical). Analysis of a 1ppm standard gave an instrument capability index of 1.55 (for n = 10), meaning that the instrument is of medium capability. The capability index, Cp, shows how well a process or instrument is able to meet specifications. It is obtained from the quotient of allowable range/6*standard deviation. A Cp value less than 1 implies that the process is unsatisfactory, a value between 1 and 1.6 implies that the process of medium relative capability while a value greater than 1.6 implies that the process is of high capability [17, 18, 19]

The uranyl, UO_2^{2+}, species concentration was determined by Cathodic Adsorptive Stripping Voltammetry using the Metrohm potentiostat/galvanostat (Metrohm PGSTAT 12) with General Purpose Electrochemical System software and a model 663VA stand (Metrohm). A multimode electrode (Metrohm, cat. No 6.1246.020) was employed as the working electrode in the hanging mercury electrode mode. A silver/silver chloride electrode and graphite electrode (both Metrohm) were used as reference and auxiliary electrodes, respectively.

An optimized method [20] for the direct determination of UO_2^{2+} by adsorptive stripping voltammetry (AdSV) using chloranillic acid as a complexing agent was used. All AdSV measurements were carried out in the differential pulse (DP) mode using a pulse amplitude of –50 mV, a pulse time of 30 ms and a potential step of 4 mV. A stock solution with 1g/L uranium was prepared by dissolving 2.1526g of uranyl nitrate in 1L of de-ionised water. Further dilutions were made every week. The concentration of the chloranilic acid solution prepared every week was 0.01M. For the voltammetric determination, a chloranilic acid concentration of 2.4×10^{-4}M, a pH of 2.4 (±0.1) and an accumulation potential of +100 mV were used. In general, no sample pretreatment was necessary except when the U concentration was too high, the sample had to be diluted so that the linear concentration range would not be exceeded by adding the standards.

Sediments and tailings dumps material for ICP analysis of total metal concentration were digested with aqua regia (a 3:1 mixture of hydrochloric and nitric acids).

Digestion was done using an Anton Paar Multiwave 3000 SOLV Microwave Sample Preparation System. Fractionated metal portions in the samples were extracted using the BCR (European Community Bureau of Reference) three-step sequential extraction procedure and then determined using the ICP-OES [21]. Sample centrifugation was done using an MSE Mistral 1000 Centrifuge.

The most important anions were determined using the Metrohm 761 Compact Ion Chromatograph with a Metrosep A Supp 5 (6.1006.520) 150 x 4.0 mm analytical column.

All solutions were prepared with purified water obtained by passing deionised water through a Milli-Q-water purification system. All chemicals were of analytical grade obtained from Aldrich, Industrial Analytical and Merck.

Chemometric data evaluation was done using QC Expert (Trilobyte Ltd) software. Speciation modelling was done using SolEq (Academic Software) and Geochemist's Workbench (Rockware) software.

5. RESULTS AND DISCUSSION

5.1 PHYSICAL SETTING

The study area (Figs. 2 and 3) covers the Simmer and Jack gold mine (west of Germiston) where large mine tailings dumps are undergoing reclamation. The artificial streams from this site drain into the adjacent Natalspruit stream. To the west of this area is the Rosherville dam which lies in an area replete with tailings dumps. It has a huge wetland which is heavily vegetated by *Phragmites* spp. reeds adjacent to it. The tributary streams to the dam pass through the wetland. Further to the west are the City Deep and Crown mines. Here samples from catchment streams and spillages or paddocks were collected. Samples from tailings footprints were also collected and analysed.

To the east of Germiston are some catchment streams that supply the Elsburg dam, Angelo Pan, the Boksburg and Cinderella dams. To the south is the Victoria Lake (a recreational lake). Further south the Natalspruit passes through residential and industrial areas before joining up with the Elsburgspruit in a huge wetland in Roodekop.

5.2. GEOCHEMISTRY

A white crust spreading several tens of square metres was observed during the beginning of the wet season sampling in a stream draining into the Rosherville dam. The crusts were more abundant in the vicinity of a reclaimed tailings dump. These crusts were due to capillary evaporation and effluorescence above a shallow water table (potential evaporation is about 1600mm/annum). A previous study [4] of similar crusts revealed that they contained gypsum ($CaSO_4.2H_2O$). Analyses gave high concentrations of heavy metals (concentrations over 1000ppm), particularly Fe, Co and Zn. The stream water and ground water in the area showed very high concentrations of U (VI). A concentration of up to 33ppm of U (VI) was recorded in the ground water. Low pH values (3.5) were recorded (Table 1).

The sediments and tailings dump material showed elevated concentrations of U and other heavy metals. Significant amounts of U can be leached from exposed mine tailings by rain water or reclamation water. During the weathering of uraninite and brannerite, a series of secondary minerals including U (VI) oxyhydroxides, silicates and sulphates is precipitated. These secondary minerals then constitute source phases for U mobilization. U is regarded as a proxy for transuranic actinides which are often found at the same contaminated sites as U. It can be present either as:

a) dissolved species in the pore water (as the uranyl ion, UO_2^{2+}),

b) adsorbed onto reactive mineral surfaces (as is the case in coatings on the tailings dumps, or

c) precipitated in discrete U containing mineral phases (such as oxyhydroxides, silicates and sulphates as is the case mainly in sediments) [2, 3].

In the BCR three-step extraction protocol for sediments, high concentrations of U, Fe, Mn, Al and S were observed. γ-spectroscopy measurements on the tailings dump material generally gave higher concentrations of ^{238}U compared to the ICP-OES measurements. In contrast, in several sediment samples from Rosherville dam, U determined by gamma spectrometry was lower than that determined by ICP-OES (Fig. 4). ^{232}Th concentrations (Table 2) were relatively low and results for both methods did not show striking differences thus indicating that this element remains in decay equilibrium under all conditions in the study area, reflecting the general chemical immobility of Th and its daughter products.

5.3. RADIOACTIVE DISEQUILIBRIA

The discrepancy in the determination of U by the different techniques is as a result of γ-spectrometry being able only to determine the U indirectly, from progeny which emit a strong γ-line, that is, ^{214}Bi and ^{214}Pb (Fig. 5) [19]. These two radionuclides are also relatively immobile compared to U and so will tend to accumulate in the outer layers of the tailings dumps. In undisturbed geological systems, the nuclides of the decay chain are in radioactive equilibrium, that is, they show the same decay rate or activity. The equilibrium is lost if geochemical processes lead to decoupling from the decay series or differentiation between chemical elements. This is the case, for example, when weathering, leaching, crystallization or precipitation occurs [22].

The tailings dumps are generally oxidized on the outside (yellowish-reddish colouring) while the inside consists generally of reduced material (the greyish pyritic material). The γ-spectrometry gave higher concentrations of ^{238}U compared to the ICP methods (Fig. 4). Samples A1 - A6 are from mine tailings dumps, A2 was taken at a tailings footprint after a rain shower. Extreme leaching was observed in sites A4 and A5. Samples A7 -A12 are sediments from wetlands. In these samples, U determined by ICP-OES is equal to or higher than that determined by gamma spectrometry. The wetlands are more than 500m from the tailings dumps and are developed along a stream that drains from the tailings dumps.

Obviously, in this case there is radioactive disequilibria since it is evident that U leached from the upper zones of the dumps while the relatively immobile Ra and Th precipitated. In the oxidized parts of the dumps, the secondary minerals, most commonly amorphous ferric hydroxide $Fe(OH_3)$, goethite (α-FeOOH) and ferrihydrite ($Fe_5HO_8.4H_2O$), usually replace sulphide minerals, resulting in thick alteration rims which surround an inner core of unweathered sulphide minerals. It is important to note that Fe and Mn co-precipitates can adsorb significant amounts of heavy metals including the radionuclides Ra and Th. The time required for the restoration of the equilibrium depends on the half lives of the involved nuclides. For instance, it will take geological time scales to re-establish decay equilibrium between ^{238}U and ^{226}Ra because of the long living ^{238}U daughters ^{234}U ($T_{1/2} = 2.5*10^5$ years) and ^{230}Th ($T_{1/2} = 8*10^4$ years); whereas the balance between ^{226}Ra and ^{222}Rn ($T_{1/2}$ = 3.8 days) is rebuilt in about two weeks [22].

In the wetland sediments, lower concentrations of Th were observed compared to the tailings dumps. Since Th is not very mobile compared to U this trend is expected because the wetlands are at a distance from the dumps. In instances where higher than expected concentrations of ^{232}Th were observed in the wetlands (for example in sample A11), this could be attributed to surface erosion from tailings dumps and consequent deposition in the wetlands. U concentrations were generally elevated in the wetlands sediments. This can be attributed to complexation with organic ligands, precipitation by reduction to U (IV) and co-precipitation.

The results reported here are preliminary, and further studies of U distribution in tailings dumps are required which will involve a systematic sampling protocol of oxidized and unoxidised material. The U concentrations will then be compared to the rate of Fe oxidation down the profile (Fe^{3+}/Fe^{2+}). Determination of Ra as a tracer for disequilibria will also be vital.

The measurements of radioactivity in the tailings dump samples give an insight into the underlying geochemical processes occurring.

5.4. SURFACE AND GROUND WATER

The ground water along the Natalspruit and in the proximity of the Rosherville Dam was characterized by low pH, high conductivity, high sulphates, U and other metals concentrations (Table 1). Of particular interest were the surface and ground water samples collected from a stream, CDX (near CD4), that drains into the Rosherville Dam. Sampling was done after a shower in the proximity of a reclaimed tailings dump. About 2.5ppm U (VI) was observed in the surface water while up to 33ppm was recorded for ground water. Gypsum crusts covered the vast area between the tailings dump and the stream. This was strong evidence of acid mine drainage and surface evaporation (Table 1). The ground water demonstrated a capacity to preserve low pH, high redox potential, sulphate and metal concentrations compared to surface water. Consequently, precipitation and dissolution reactions are important processes in controlling the chemistry of groundwater. Dilution effects in the case of surface water tend to result in near-neutral pH and lower concentrations of sulphates and metals compared to ground water. However in streams near tailings dumps, the pH remained relatively low and metal concentrations high (Tables 3 and 4). CD 8 is surface water in a tailings dump undergoing treatment. Elevated U (VI) concentration (13.8ppm), other metals and SO_4^{2-} concentrations (>7000ppm) were recorded. A high redox potential was also recorded (764mV) indicating that the reclamation process exposed much of the material to oxidation. CD 9 is water from a stream draining directly from the tailings dump. Although its pH is low, it shows notable attenuations of the metal and SO_4^{2-} loads implying that some precipitation occurred along the path. This can be attributed to the effects of dilution, oxidation of Fe and the subsequent formation of metal-scavenging oxyhydroxides. In the distal reaches and particularly in wetlands the pH increases and the metal concentrations are attenuated drastically in the surface water (for example, streams such as CMR1, CMR2 and CMR3 in Table 3 and NPU and NPL in Table 4 are at some distance from tailings dumps). The ground water from Simmer & Jack mines exhibited low pH and elevated concentrations of U (VI) and SO_4^{2-}. The stream water on the other hand gave lower concentrations as a result of dilution. Dams showed near neutral pH and very low concentrations of U and other metals (for example in Table 4, samples BD, CD, ED and VL are samples from dams). This could be attributed to the effects of neutralization and dilution of acid drainage. This is expected since sampling was done at the beginning and end of the rainy season (September and May respectively).

5.5. WETLAND SEDIMENTS

Wetlands are those areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions. Wetlands generally include swamps, marshes, bogs and similar areas [23].

It is now widely accepted that, to assess the role of wetland sediments as sinks or sources for heavy metals, the measurement of the total content must be integrated with the determination of metal partitioning among the different sediment phases. In fact, it is necessary to obtain information on the potential availability of metals (whether toxic or essential) to biota under various environmental conditions. The behaviour of metals and their availability strictly depends on their chemical form, and thus on speciation [22]. The determination of the chemical form or kind of association with different mineralogical phases in sediments is thus important. The phases determine the intrinsic toxicity of the host matrix (soils or sediments) as well as the mobility potential of metals in the environment to either surface or ground waters, living organisms (plants and meso-fauna) or to the atmosphere.

The BCR sequential extraction protocol on profiles in wetland sediments showed high concentrations of metals such as U, Fe, Al, Ca, Mn, Co and Zn and non-metals such as S. This method gives biogeochemically relevant fractionation of metals in sediments and soils. It differentiates metals into behavioural classes, that is, acid-soluble, reducible and oxidisable fractions. The first step involves leaching with acetic acid. This targets the water and acid-leachable metal fractions. The second step uses hydroxylamine hydrochloride on the residue of the first step and this removes the metals bound to oxides. In the third step, oxidation with hydrogen peroxide followed by reaction with sodium acetate is done on the residue from step two. This targets the metals bound to sulphides and organics [21]. High concentrations of the metals were observed to be associated with the reducible fraction or oxides/oxyhydroxides of Fe and Mn and the oxidisable fraction or sulphide/organic fractions (Table 5). The acid soluble fractions are the most mobile and determine the bioavailability of the element. U was observed to associate more with oxides and sulphides/organics (Fig. 5). On average, over 50% of U in the samples is bound to oxides. Fe and Mn show high association with oxides, further highlighting that they form the bulk part of the oxides and consequently co-precipitate other elements with them. Results from aqua regia extraction were comparable with those for BCR extraction. Aqua regia is a 3:1 mixture by volume of $HCl:HNO_3$. Its dissolving power is derived mainly from the ability of chlorine and nitrosyl chloride to oxidise the metals which are then transformed to stable complex anions by reaction with the chloride ion [21].

During acid mine drainage formation, Fe^{2+} released from the sulphide oxidation can be further oxidized to Fe^{3+}. This Fe^{3+} may be hydrolysed and precipitated as $Fe(OH)_3$ or a similar ferric hydroxide (for example, goethite) or hydroxyl-sulphate:

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$$

The $Fe(OH)_3$ acts as a strong sorbent for many trace elements in aqeuos systems. Its ability to trap dissolved species during co-precipitation has been utilized in the purification of drinking water. During the precipitation of hydrous ferric oxides, U is also scavenged [22]. The approximately constant U/Fe ratio (for oxide-bound fractions) in the sediment layers strongly suggests that the stability of U immobilization is linked to the stability of the hydrous ferric and Mn oxide precipitates (Table 5).

The high sulphate loads in the water precipitate as sulphates in the wetlands (acid leachable S in Fig. 6). The other sulphate portion is reduced by sulphate-reducing bacteria which are ubiquitous in the wetlands thus leading to the precipitation of metal sulphides. Bacterially mediated reduction of sulphate can be expressed as:

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O,$$

where CH_2O represents organic carbon. In the presence of soluble metals, hydrogen sulphide can react to form sulphides;

$$Fe^{2+} + H_2S \rightarrow FeS_{(s)} + 2H^+$$

Elements such as As, Cd, Co, Cu, Ni, Pb and Zn can also react with H_2S to form sparingly soluble sulphide minerals. This reaction sequence results in decreased concentrations of dissolved SO_4^{2-}, Fe, and other metals. The geochemical conditions in the wetlands support the reducing conditions necessary for sulphate reduction. On average, over 60% of S in the samples was in the sulphide form. The acid leachable form are the sulphates. Al has a tendency of forming oxyhydroxides like Fe and Mn and so its high concentrations were recorded as associated with oxides.

Complexation reactions occur between most metals and organic substances such as humic acids (fulvic and malonic acids) which are present in wetlands. Under weakly acidic conditions typical of wetlands, the chemical speciation of uranium may become dominated by the formation of stable complexes with soil organic matter. This commonly results in the retention and accumulation of U in peat deposits, although in situations where a significant proportion of organic matter is in the dissolved form this may assist in the dissolution and mobilization of soil-bound U. U is also reduced by microbial activity in wetlands thus leading to the formation of UO_2. In addition to transport in the dissolved phase, labile U may also be redistributed from soils and sediments into the water courses and surface water reservoirs as, or sorbed onto, particulate matter during storms and other modes of physical erosion [3, 23].

5.6. EVALUATION OF DATA

5.6.1. MAPPING OF RESULTS

Contour mapping was used to assess trends in uranium distribution in the Central Rand (Fig. 3). Generally, high concentrations were observed in the vicinity of the tailings dumps and active slimes. Concentration was found to be a function of the activity in the dumps. There was a dramatic attenuation with distance from tailings dumps and also in areas where no retreatment activity was occurring, (for example, the CMR samples displayed very low U concentrations). No extreme U concentrations around the Rosherville dam appear on the map. This is because no activity was occurring in tailings dumps in the vicinity at the time of sampling. The high concentrations in CDX discussed above were as a result of some retreatment activity in the dumps near the area during the period of sampling.

5.6.2. CHEMOMETRIC EVALUATION

Correlation matrices (using Spearman rank correlation) were calculated in order to assess the linear dependence of the variables. The QC Expert statistical software [24] was used to perform the calculations. The Spearman rank correlation is a non-parametric method that measures the correlation between two sequences of values. It is a method to test for an association between two variables [25, 26]. For water samples, U(VI) was observed to be highly correlated with Zn, Cu, Ni, Mn and Co (Table 6). It was also observed to be strongly correlated with sulphates (0.70) and conductivity. A strong correlation between Ca and sulphates (0.82) was observed thus showing a strong association between the two ions in the aqueous system.

5.7. GEOCHEMICAL MODELLING

Modelling allows us to draw conclusions, or predict from the measured data, or make more precise statements about the nature of the underlying data relationship. In this sense, a model creates the capability of prediction. A geochemical system consists of a set of primary chemical species, and the aqueous complexes, minerals and gases. Reactions between aqueous species (homogeneous and heterogeneous) are assumed to be in equilibrium [27, 28].

Modelling of U distribution in ED using the Geochemist's Workbench Release 4.0 modelling software gave the Eh-pH diagram in Fig. 7. With a pH of 6.7, redox potential of 585mV and U concentration of about 4ppb, the U exists mainly as UO_2OH^+ in this sample. At very high pH values, it is anticipated that UO_2^{2+} will exist mainly as a uranyl-carbonate species. These complexes are very soluble and contribute significantly to the mobility of U in water exposed to mine tailings. Below pH 5, UO_2^{2+} is an important species [29].

The Eh-pH diagram summarizing the fundamental reactions of U in sample CDX (sample of extreme conditions) is given in Fig. 8. From the diagram, U exists mainly as the uranyl-disulphate complex. Redox potential and pH affect, significantly, the solubility of heavy metals and the type of species these metals form [30]. The occurrence of U and SO_4^{2-} in ground and surface water indicates that uranyl-sulphate species are important for the understanding of the mobility of U in nature [31]. From the model, U is found in the uranyl-disulphate form till above pH 8 where its hydrated form plays an important role. SolEq modelling (Fig. 9) predicts, for the same sample, U speciation as a number of uranyl-sulphate species depending on pH. Though the model identifies the presence of the hydrated species (up to 23.2%) and the sulphate-complexes, it does not identify the presence of other species such as schoepite and uraninite.

The ground water samples CDX, RD, SJ2G and SJ5G were plotted together with the surface water CD8 (Fig. 10). The uranium in these samples exists in the UO_2^{2+} form, except in RD where the model shows it to exist in the form of schoepite. This could be attributed to the low redox potential that leads to reducing conditions thus precipitating some U (schoepite is the hydrated compound $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$). U exists as uraninite (UO_2) in highly reducing conditions [32, 33]

6. CONCLUSIONS

The legacy of gold mining activities around Johannesburg consists of enormous heaps of tailings dumps extending over many square kilometres. These sites must be considered as potential sources of mobile uranium to the biosphere. Gamma spectrometric analysis points to significant leaching of U from tailings dumps. This has caused some radioactive disequilibrium as U has been decoupled from the decay series. The international specification limit of 20ppb U(VI) in natural waters [34] has seemingly been exceeded, in some instances by over 1600 times, in most cases that were investigated in this study. Very high concentrations were obtained in water bodies in the proximity of tailings dumps whereas significant attenuation was realized in areas far from the sources. The processing of mine dumps has also contributed to enhancing acid drainage and probably oxidation of dump material, thus enhancing U mobility. Wetland sediments showed that they act as traps or sinks for U and other heavy metals, this being strongly demonstrated by BCR sequential extraction. The oxide-bound fractions from this protocol point to co-precipitation as the main U removal process from the water column. It should be noted that the toxicity of U is not as a result of its radioactive nature, but rather its chemical nature. The kidney is considered the target organ for uranium's chemical toxicity. The dissolved uranyl-complexes decompose in the kidney releasing uranyl ions which depress glomerular function, tubular secretion of filtered organic anions (these are important for sequestering heavy metals), reabsorption of filtered glucose and amino acids [35].

Because of its low solubility and high sorption tendency, Th is found in higher amounts in the tailings dumps than in the distal wetland sediments [36]. Where surface erosion or spillage has occurred, the concentration of Th is found to be higher than expected. Modelling results show that at low pH, the SO_4^{2-} species plays an important role in U speciation. Hydroxy and CO_3^{2-} species prevail at higher pH. The CO_3^{2-} species is not very common in the Witwatersrand [2] and much of it that has been observed has been assumed to come from external sources. The partially rather low observed U concentrations in some cases might indicate tetravalent U as solubility-controlling redox state. Reduction appears to be related to accumulation of organic material in the sediments.

Microbiological activity has not been studied. A future study of microbial activity effects on U behaviour in natural aqueous systems may provide interesting insight for understanding the geochemical cycling of this element [37].

ACKNOWLEDGEMENTS

The authors would like to thank the National Research Foundation (NRF) for the financial support of this research study.

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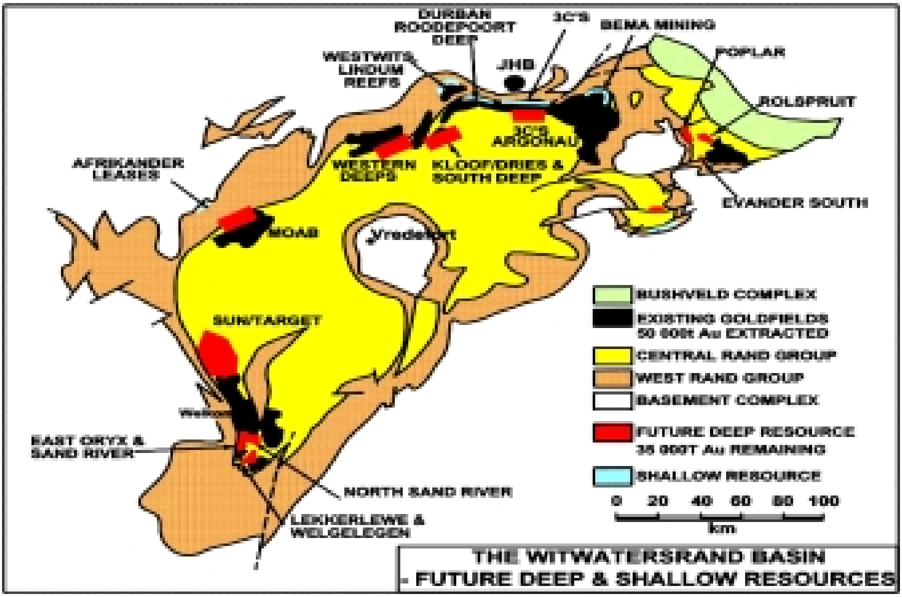


Fig. 1. Map of the Witwatersrand Basin

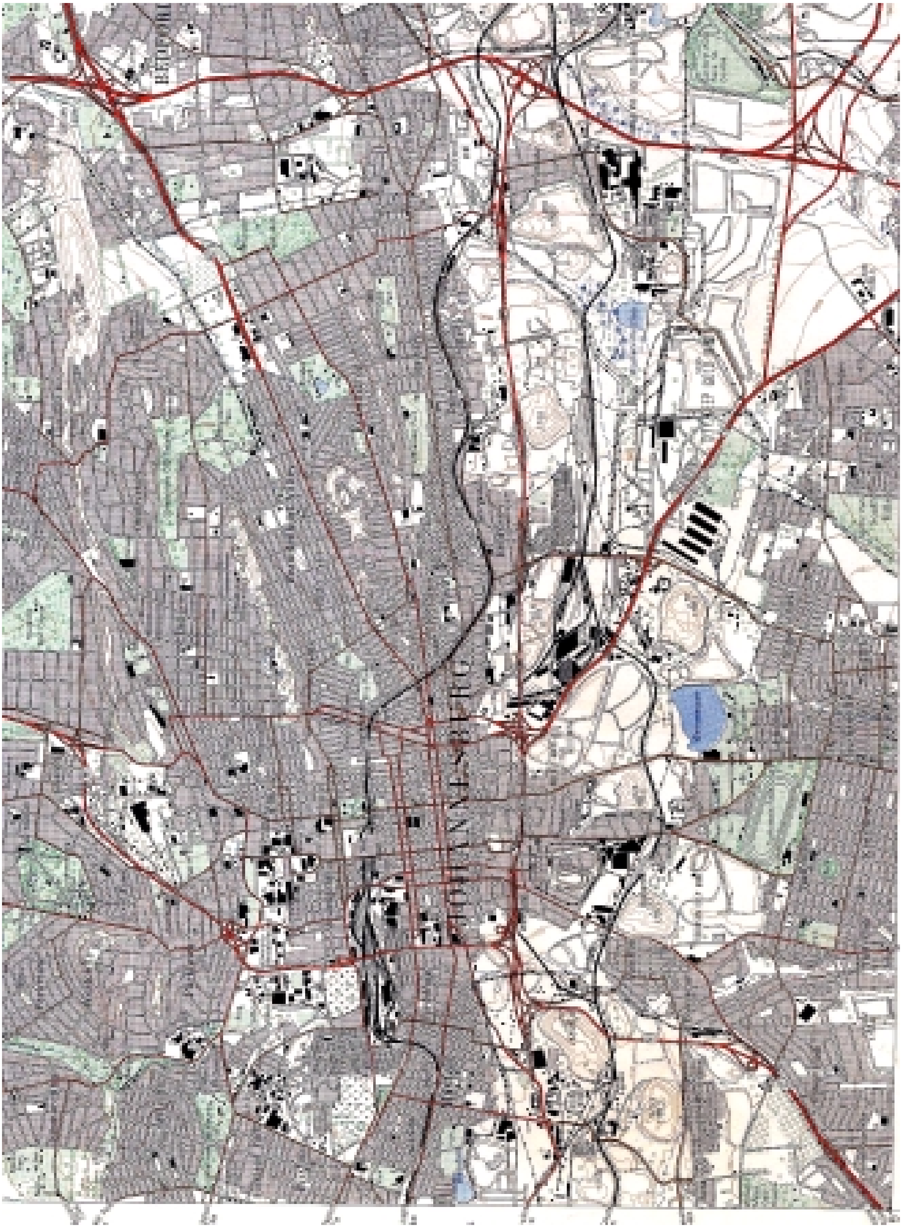


Fig. 2. A map of the study area showing the East Rand and part of the Central Rand.

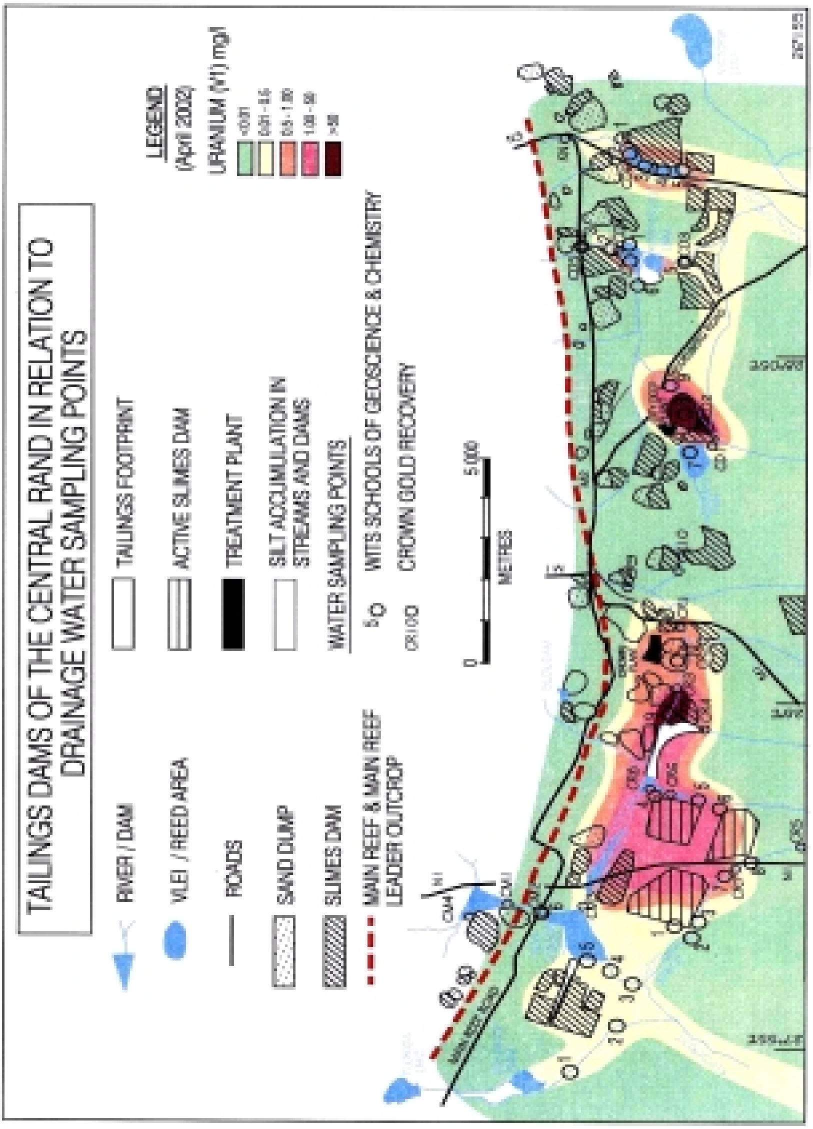
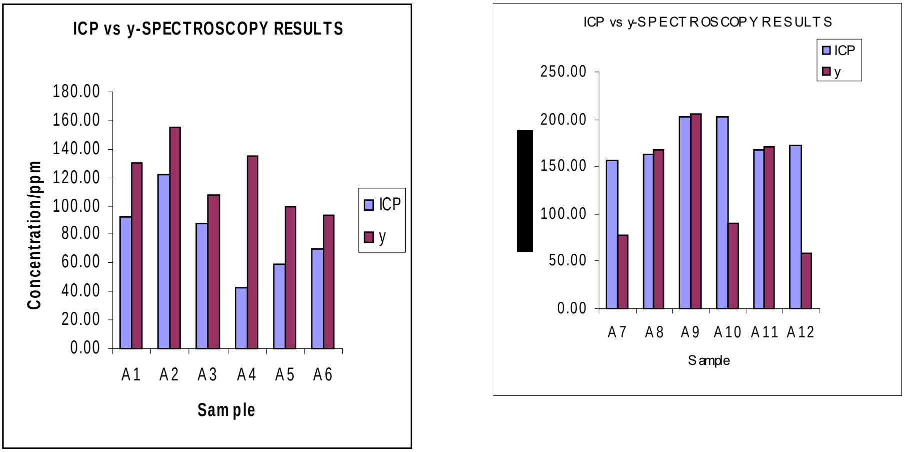
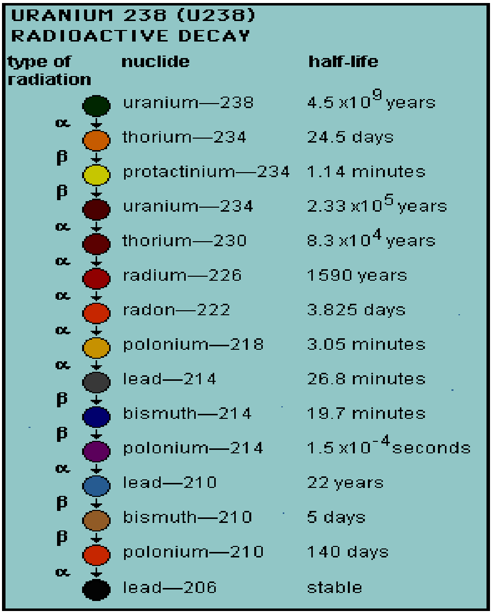


Fig. 3. A contour map for total uranium distribution in surface water in the Central Rand.



a) *b)*

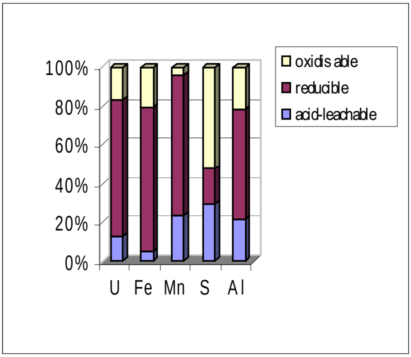
Fig. 4. Comparison of ICP-OES and γ-spectroscopy results for uranium in (a) tailings dumps and (b) wetland sediments.

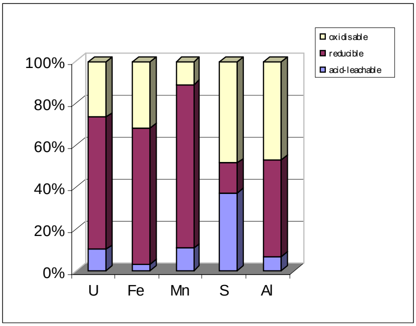


URANIUM 238 (U238)
RADIOACTIVE DECAY

type of radiation	nuclide	half-life
	uranium—238	4.5 x10^{9} years
α		
	thorium—234	24.5 days
β		
	protactinium—234	1.14 minutes
β		
	uranium—234	2.33 x10^{5} years
α		
	thorium—230	8.3 x10^{4} years
α		
	radium—226	1590 years
α		
	radon—222	3.825 days
α		
	polonium—218	3.05 minutes
α		
	lead—214	26.8 minutes
β		
	bismuth—214	19.7 minutes
β		
	polonium—214	1.5 x10^{-4} seconds
α		
	lead—210	22 years
β		
	bismuth—210	5 days
β		
	polonium—210	140 days
α		
	lead—206	stable

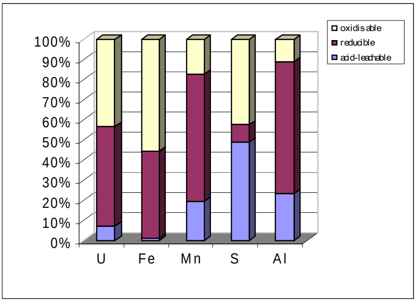
Fig. 5. The Uranium-238 radioactive decay series (Note: Each α and β decay is accompanied by a γ-emission. For ^{238}U, the near-end progeny, for example, ^{214}Bi and ^{214}Pb display a strong γ-emission.)

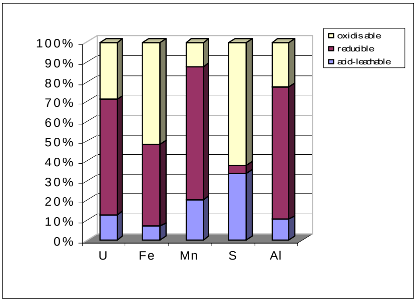




a) CDX2A

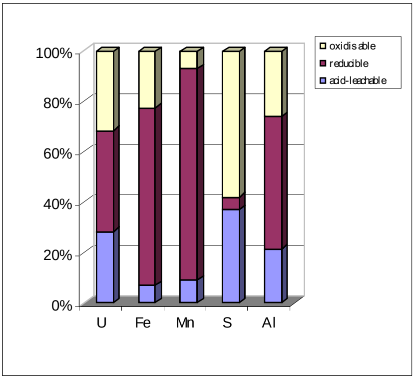
b) CDX2B





c) CDX2C

d) CDX2D



d) CDX2E

Fig. 6. BCR sequential extraction results for U, Fe, Mn, S and Al in five sediment profiles.

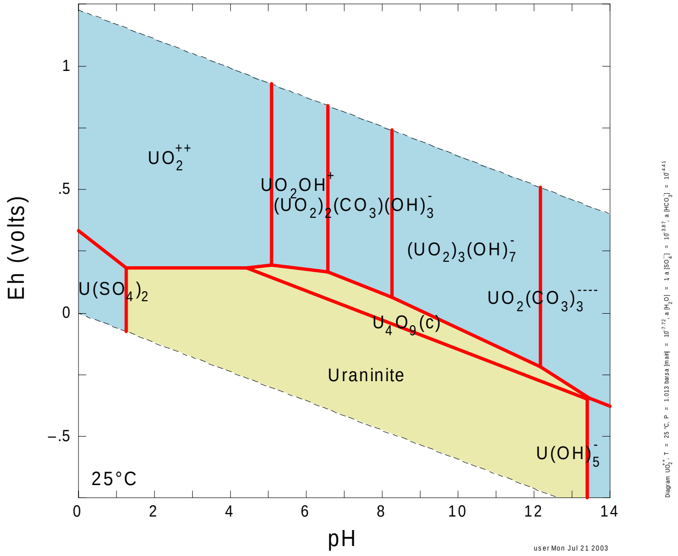


Fig. 7. Eh-pH diagram for uranium distribution in ED (the enclosed area indicates limits of natural environments). Carbonate concentration for this sample was determined by titrimetry as 1.38mg/L

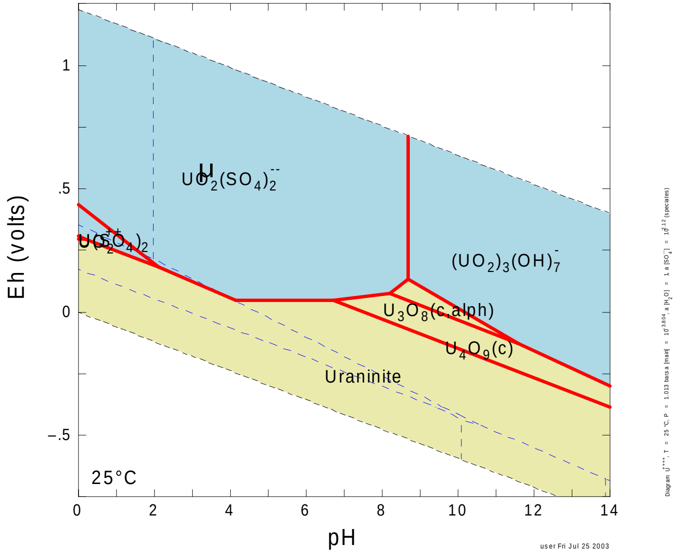


Fig. 8. Eh-pH diagram for uranium speciatiation in CDX ground water (the enclosed area indicates limits of natural environments). X – samples..

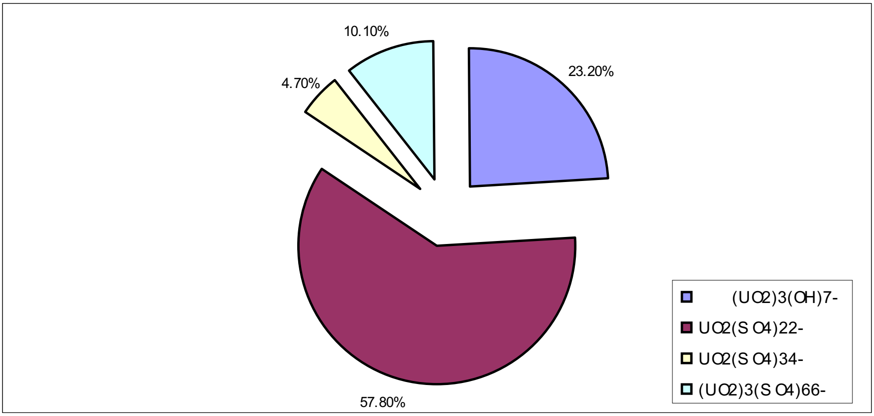


Fig. 9. Pie chart showing U speciation in CDX using SolEq

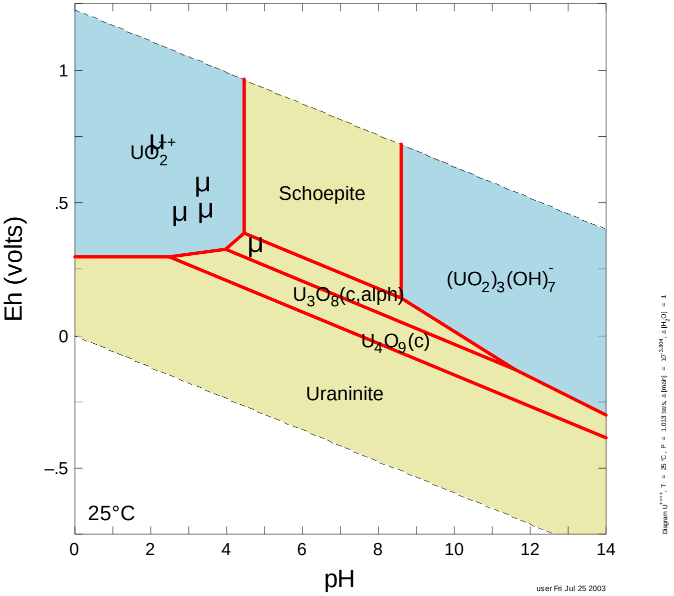


Fig. 10. Eh-pH diagram for uranium speciation in ground waters CDX, RD, SJ2G, SJ5G and surface water CD8 (the enclosed area indicates limits of natural Environments). X – samples.