NÁSLEDKY HYDROMETALURGICKÉHO ZPRACOVÁNÍ URANOVÝCH RUD V OBLASTI BÝVALÉ ÚPRAVNY MAPE - MYDLOVARY U VODŇAN

CONSEQUENCES OF URANIUM ORE WET METALLURGY PROCESSING IN MAPE - MYDLOVARY AREA AT VODŇANY

Jaroslav ŠVEHLA
[1]Jihočeská universita v Českých Budějovicích, Department of Applied Chemistry, Studentská 13

Souhrn
Článek podává stručný literární přehled o principech hydrometalurgického zpracování uranových rud a následných problémech s tím spojených. Na několika příkladech chemických úpraven uranových rud (Stráž pod Ralskem a MAPE Mydlovary) uvádí výčet hlavních problémů (emise prachu a radonu) a škod na životním prostředí (kontaminace spodních vod), možnosti sanací, rekultivací a následného využití oblastí poznamenaných těžbou a chemickým zpracováním uranových rud. Závěrem jsou nastíněny možnosti nápravy způsobených problémů a rámcový odhad jejich časové a finanční náročnosti.

Summary
This literature review deals with principles of uranium mining with wet metallurgy, and some related problems. Two examples of uranium mill tailings from Czech Republic (Stráž pod Ralskem a MAPE Mydlovary) are introduced with their main problems in environment damage (dust and radon emission, groundwater contamination), possibilities of sanitation, reclamation and revitalization of areas contaminated like that. In conclusion there is outline of some possibilities of problems reparation and time and money estimation.

Key words:
mining, uranium mill tailings, radon, dust, groundwater contamination, reclamation

Introduction

Uranium is one of actinoids (Z = 89-103) of which all known isotopes are radiocative. Half-life of most actinoids is too short so that only ^{232}Th, ^{235}U, ^{238}U and probably ^{244}Pu could have survived since the Solar System has been formed (Greenwood, 1993). Some other isotopes, which originate by means of continual processes of radioactive transformation in equilibrious trace quantity may be assigned to these ones. ^{234}U is the most important among them (with half-life of $2.45 \cdot 10^5$ years), which, however, makes up only 0.0054 % of all the three natural isotopes of uranium. Average content of uranium in Earth's crust is estimated to 2.3 ppm, which means uranium is a bit more abundant than e.g. tin. It is rather widespread element and because it has probably crystallized later during formation of igneous rocks it is often found in defective belts of older rocks of crystalinicum. A large number of oxidical minerals, of which black blende or uraninite U_3O_8 and carnotite $K_2(UO_2)_2(VO_4)_2*3H_2O$ are the most important, have been formed by leaching out and re-condensing followed by concentration. These materials, however, are considerably scattered in rocks so that typical uranic ores reach approximately up to 0.1 % of U (Greenwood, 1993).

In second half of the past century fall in prices was caused by overproduction and accumulation of natural uranium reserves, which was no longer demanded. Collapse of final product market - so called „yellow cake" (diuranate ammonium) followed, decrement in mining and seeking for sanitation and supplementary manufacturing programmes occurred in most of world deposits. Former uranium mine with mill tailing at Driefontein in Southern Africa, for example, was successfully transformed into plant for getting gold from old bingsteads of waste rock (Buson et al., 1999). Price of uranium in the world market, however, raise, which is why also in our country re-opening of mining in some of closed mines or even opening new ones starts to be considered (Lepka, 2003, Kubátová, 2007).

Development of uranium price at the world market

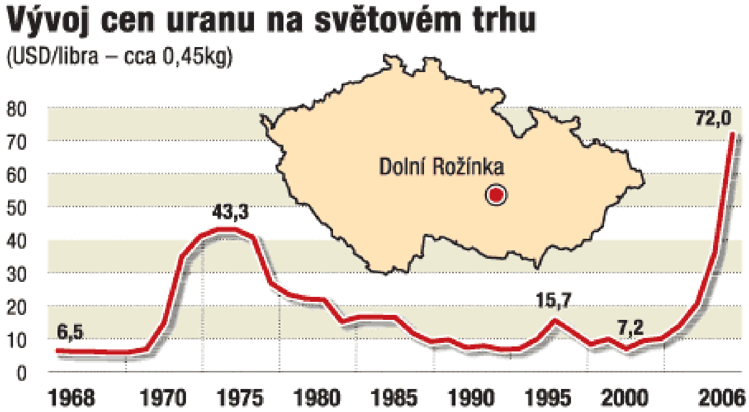

Figure 1: Development of uranium price at the world market (Kubátová, 2007)

Getting uranium from ores

Uranium is got from ores with average content of approx. 2 kg U/t in chemical mill; the ore is thoroughly ground to a very fine granularity (< 0.1 mm). Usually acidic or alkaline leaching and separation of pure tinctures follows, finally uranate is condensed by ammonia in the tincture. Insoluble remnant of crushed ore (green ore leached out - mash - sediment) contains, besides residual quantities (approx. 1/10 of its original one) of uranium, which was not leached out, also complete original content of especially supporting radium and other, yet non-radioactive but highly toxic elements (Tomášek, 2001). Green ores leached out this way are then pumped off and stored in storage area where they should be stored forever. Problems usually occur in this stage because sediment and remnants of leaching solutions usually still have very acidic reaction (pH ranges from 1.5 to 3.5) and besides high concentration of radioactive isotopes of radium, thorium and uranium there is also mostly arsine, beryllium, cadmium, chromium, plumbum, molybdenum, nickel and selenium. Perfect leakproof subsoil of such reservoirs is prerequisite for safe storage of such materials in order no degradation of sources of ground water in surroundings may occur (Zhu et al., 2002).

Consequences of uranium ores processing

After drain of storage area lagoons other problems occur, especially those with dustiness and unsuitable physical and chemical properties of the sediment for vegetation growth (Jim, 2001). In case any vegetation takes roots in areas like that it is potentially toxic - for high content of accumulated radionuclides and heavy metals and it causes further diffusion of toxic elements to food chains. Bio-accumulation ability of some plants may, however, be used for phyto-remediation, i.e. absorbing toxic elements from contaminated soil; e.g. some kinds of resistant grass are able to selectively accumulate only selenium, which may be used as food supplement for animals in areas with lack of selenium (Sharmasarkar et al., 2002).

Another serious problem, which is difficult to be solved, is gaseous emissions (emanation) of radon and following contaminant fall-out of its solid radioactive daughter products of uranium desintegration chain in drained storage areas. These daughter products have rather short half-lives and they finish by stable isotope of plumbum ^{206}Pb, which has accumulative toxic effect like other toxic heavy metals. Especially risk of bio-accumulation in bodies and organs of organisms, specifically gradual growth in concentration in food chains is important as far the type of radioisotopes of trace elements of metallic nature is concerned. Concentration of ^{222}Rn in outer environment usually ranges within interval of 3.7-18.5 Bq/m^3, average for the Czech Republic is set approximately 5.5 Bq/m^3 (Tomášek, 2001). In accordance with decree of SÚJB no. 307/2002 Coll., the limitary activity of ^{222}Rn inside buildings ranges within 100 and 200 Bq/m^3. Up to 420 Bq/m^3 was metered in the air in storage area at uranium mill tailing MAPE Mydlovary in the Czech Republic during completion activities (Hanslík, 1991).

Situation in the Czech Republic

It was continued in mining and processing uranium ore in our country, in former socialist Czechoslovakia, as well as in entire RVHP only on empty as a consequence of Cold War for about ten years longer than in the world, i.e. till mid-nineties. There were about five main deposits of uraninite at territory of Bohemia and Moravia: Jáchymov, Příbram, Okrouhlá Radouň, Dolní Rožinka and Stráž pod Ralskem.

In the last place, uranium has been got also in so called „chemical exploitation“ since 1974; i.e. forcing leaching solution of sulphuric acid through deep wells directly to uraniferous horizon in Cenoman formation. Leaching solutions penetrated the rock, leached uranium and were drawn back through production wells. Uranian compounds were then separated from these tinctures, which were processed into final product - „yellow cake“. After the solution was cleared from uranium it was acidulated with sulphuric acid and repeatedly forced in the underground. About 8,000 technologic wells were made through which over 4 million tons of sulphuric acid, 320 thousand tons of nitric acid and thousands of tons of other chemicals were forced in the underground till closing mining on March 31, 1996. Process of acidic leaching is said to be then the largest in the world. Over 15 thousand tons of uranic concentrate was produced and exported to former USSR. Chemical mining caused extensive contamination of ground water and in smaller extension it also influenced soil, countryside and atmosphere here. At the present time (2006) the aquiferous Cenoman collector lies on area of 24 km^2. Contamination of mass surroundings caused by chemical mining potentially endangers sources of drinking water as well as surface water in the region. There is danger of transfer of very acidic and alkali solutions to Turonský collector of ground water, which might degradate valuable water sources - the biggest ones on the Czech Republic - for several centuries. This is why it is necessary to carry out sanitation of this area. According to model calculations sanitation and liquidation of consequences of chemical mining of uranium will take about 49 years and the costs will be about 40.9 billion CZK (Josefi a kol., 2006).

There is 286 ha of uranium storage areas together with former uranium mill tailing called MAPE Mydlovary (name of chemical used: MAnganese PErchlorate) in Southern Bohemia not far from Hluboká nad Vltavou among Mydlovary, Zahájí, Olešník, Nákří and Dívčice municipalities. Uranic ore has never been mined in this area neither in its surroundings. It has been transported to MAPE from uranic mines from nearly all the country and sometimes also from abroad. Sediment fields were largely formed in space made by lignite mining, which had been mined here since nearly beginning of the last century for Mydlovary power station, which was lately used only as a heating plant. The uranium mill was originally designed to process 300,000 tons of uranic ore a year. Trial run of so called acidic line was started in October 1962 and the one of alcaline line in April 1963. The intended performance was reached as early as by the end of 1963. Ores with higher content of carbonates (Rožinka, Příbram) were leached in soda (alkaline line) and ores with low content of carbonates (Chodov) in sulphuric acid (acidic line). After beginning of mining in Hamr deposit in Northern Bohemia the acidic line was also divided to hard one, where leaching was performed in high concentration of acid. Technologies of uranium processing from all Czechoslovak deposits of uranic ore were gradually developed and realized at the mill. Processing capacity reached its maximum between 1979 and 1983, when over 700,000 ton of ore was processed a year. After 1988, reduction of sales of uranic concentrate occurred and as a consequence of continuous falloff of mining and processing of uranium its processing in uranium mill tailing Mydlovary stopped in October 1991; more than one year before schedule approved by government of ČSFR in its resolution no. 894/1990. During its activity MAPE plant produced over 17,000,000 tons of uranic ore and produced about 36,000,000 tons of sediment. Sediment volume - 24,000,000 m^3, water bound volume - 17,000,000 m^3 (Tomášek, 2001).

During activity of MAPE plant about 36 mil. ton of sediment was produced, which was hydraulically transported do storage areas with its total area of 286 ha. The storage areas are not only hazardous waste dump but also water constructions of category III and IV. Important contaminants of the storage areas are emissions of dust, volume capacity of radon and gamma radiation (P.Bossew, 1991). It is obvious, according to results of monitoring of state of environment that Mydlovary storage area negatively influents especially quality of air and ground water. Dust fall-out in the area of question is approx. 30 per cent higher than in reference point at Hluboká nad Vltavou. Either drying beaches of slush pits, which are source of radio-nuclides or secondary dustiness caused by bank of reclamation materials to the storage area is the originator of this pollution. Volume activity of radon in protection zone of storage areas is significantly higher than background value and in dependence to climatic conditions maximum admissible concentration of radon in inbreathed air in this area is exceeded (Diamo, 1998). Waste from MAPE makes up source of possible long-term radiation influence to environment, which requires its regulation by suitable retention and closing. 226-radium concentration in soil samples besides the plant exceeds 10,000 Bq/kg and background makes up 60 - 80 Bq/kg (Mondspiegel a kol., 1990). Radon emission represents risk for inhabitants in the surroundings and its air transport represents risk also for other area. Radon emission to the air at the storage area, where radon concentration up to 420 Bq/m^3 was metered, whereas admissible concentrations inside buildings are 100 Bq/m^3, represents a significant load for living organisms. Diffusion of radon desintegration products to the surroundings and food chains should be restricted (Hanslík, 1991).

Besides other inhalation of radon, external exposition to gamma radiation and also arsine, beryllium and cadmium in case of hypothetical script of drinking ground water contributes to overall unacceptable carcinogenic risk of inhabitants of Mydlovary, Zahájí and Olešník municipalities as it is mentioned in Process of evaluation of MAPE influences to environment and suggestions of their minimization (EIA, Tomášek 2001). Moreover, from point of view of carcinogenic risks there is also danger of inhalation of manganese compounds from the air in Olešník municipality.

According to a thirty-year monitoring of causes of death in one of close municipalities there is a significant increase in occurrence of tumours, which causality with MAPE plant cannot be excluded (Reban, 2006). Toxicity of flow water below K-III storage area flowing in Svatopluk sewer in front of Olešník (Máchová, 2006) was proved in 2006. Uranium etc. release into biosphere may be proved for example with mere comparison of its average concentrations in surface water of Sodný and Dehtářský creek or with use of some of sensitive bio-indicators even in middle part of Vltava (Tykva et al.).

The only up-to-date official source of information about progress of sanitation and reclamation work and influences to environment is section periodic „Report of Diamo state enterprise on results of monitoring and state of compounds of environment in Mydlovar area“ (Starý, Mališ, Urban, DIAMO, 2006). Besides others it is mentioned here, that excession of investigation limit as for uranium is concerned in sewer water from ČOV of former MAPE plant released to Soudný creek was recorded in period of low rainfall (February 2005 up to 0.37 mg/l, but year 2001 up to 1.01 mg/l) when increased influence of infiltration of polluted water from subsoil of production plants to sewerage of former mill occurs. During releasing refined over-balance water to Vltava pod Hlubokou in 2005 water limit concentration (given by relevant Exception of OÚ Č. Budějovice) was exceeded in releasing profile but only as far as nitrites (9,63 mg/l) are concerned; at the same time over one million of Czech Crowns was paid for released pollution in accordance with Act no. 254/01 Coll., (especially for high content of inorganic salts, up to 12.7 g/litre). On May 1, 2005 sewage disposal plant (ČDV) was shut down and replaced with innovative technology of alkalinization directly in sump, which resulted in increase of quantity of water released directly to Vltava to record-breaking 284 250 m^3 (Diamo, 2006).

Quality of air in MAPE plant area and in its surroundings in comparison with previous years distinguished with cut dustiness (approximately 18 per cent of limit) and equivalent volume activity of radon (EOAR) remained at level of previous years, mainly under investigation limit approved by SÚJB Prague, i.e. 50 Bq/m^3, with its highest average values in Zbudov (11.3) and Mydlovary (10.8 Bq/m^3) municipalities. Reclamation work has to cut the radon emission to internationally recommended limit, i.e. 0.8 Bq/m^2/s, which should cut exposition of critical group of inhabitants in Mydlovary from building of former mill from present value of approx. 200 μSv/year (i.e. 20 % of the limit) to approx. 90 μSv/year (9 % of the limit).

Reclaimed area of sump made up exactly 98.5 ha at the end of 2005 out of total 286 ha, whereas total area of monitored zone is 8 km^2, including sumps (Starý, Mališ, Urban, DIAMO, 2006). There is also reference about interesting excesion of investigation limit (0.2 mg/kg) of volume of uranium in agricultural crops (barley at K-III - 0.4 mg/kg, rape at K-IV/E - 0.25 mg/kg and grass at K-I - 0.4 mg/kg) besides completely unspecific and therefore unpursuasive statement about „cutdown in content of metals in all monitored crops“ without any further specification in chapter 4.2 of the above mentioned Report on biosphere contamination. There is a question why agricultural crops are grown in vicinity of slush pits.

Certain monitoring of migration and accumulation of heavy metals and radionuklides to particular elements of environment was, still during operation of MAPE plant, carried out by Department of Ecology of then VŠZ (today ZF JU in České Budějovice) upon order of former

Uranový průmysl, s. p. (today DIAMO, s. p.), however these results were not published openly, besides marginal reference about contamination of rabbits with radium 226 and uranium (Hanslík, 1991); up to 337 Bq/kg of radium and 4.6 g/kg of uranium were found in their bones.

Possibility of rectification

The first stage of sanitation and reclamation work consists in drying lagoons and hermetic closing of area above sumps. This should result in significant restriction on outflow of radionuklides. This sanitation and reclamation work shall partly purify the countryside from negative influence of sumps, which contain a big quantity of radioactive mash, but they proceed very slowly. There is lack of sanitation materials but mainly lack of finance. Annual dump of reclamation material of 250,000 tons is expected in area of sumps in MAPE plants. Total amount of material for sanitation is estimated to about 7,036 million tons. Reclamation period was, according to suggestion of Project of Blata Municipality League in 2004, shortened form initial 40 to 28 years (Houba 2004). Overbalance sump water should have been minimized; by-pass road around Zahájí and Mydlovary and compost site should have been built etc., which was not reached probably also because even EU did not find finance for that. Supposed finance for sanitation and recreation were estimated to tens of billion CZK (Ješ, 2007).

K-III over Olešník municipality is the most hazardous slush pit from point of view of pollution of ground water according to the latest study of complex solution of contamination of ground water by soak from sump in Mydlovar area, which is to be used in a new EIA (2007-11) process. Dominant influence of the sump to chemism of ground water reaches up to distance of 900 m, i.e. to fly ash sump from former power station at Mydlovary. Average rate of progress of ground water contamination is estimated to 36 m/year upon this information. Conclusions of this study work on presumptions of mathematic model of spreading of the water contamination also suggests that further contamination may be expected in direction of Mydlovary pond at Zlivy (ENACON - Praha, 2006). Further it is also said that plugging K-III sump within planned reclamation work will be, regarding occurrence of contamination in area of permanent streaming of ground water, insufficient, which is why additional solution is suggested.

According to sanitation study of Pincock, Allen & Holt from U.S.A. elaborated recently for Diamo it is suggested to move this problematic K-III sump hydraulically to one of unflooded sumps with use of geotextile technology of sediment draining (Pincock et al., 2005).

Conclusion

The sanitation studies mentioned, however usually do not solve the last stage of the reclamation, which is planting with greenery and further countryside maintenance. This stage of reclamation is quite distant now, yet it becomes to be relevant at redeveloped K-I sump. It is not suitable to leave this last stage to natural succession of invasion vegetation since birch trees and similar seedage wood would either destroy waterproof sealing layer of the material or transport radionuklides to the environment. This is why it is necessary to look for and grow suitable herbs, which will survive in this extreme place and which will not significantly accumulate neither heavy metals nor radionuclides. This represents a wide field for collaboration with workplace dealing with phyto-remediation (Tykva a Berg, 2004).

Citations

Bossew P.: Radio-ecological investigations in the surroundings of MAPE uranium ore processing plant near České Budejovice in southern Bohemia (CSFR)., Studie rakouského ekologického institutu, Vídeň, 1990, 15 pp.

Buson G.D. et al.: The West Driefontain reclamation carbon-in-pulp plant, pilot plant testwork, design, commissioning and optimization., J. of the South African Institute of Mining and Metallurgy 99(2), 1999, 63-67 p.

DIAMO s.p.: Analýza rizik - odkaliště Mydlovary, 1998, 28 pp.

DIAMO s.p. (Starý,P., Mališ A., Urban P.): Zpráva o výsledcích monitoringu a stavu složek životního prostředí v oblasti Mydlovar., únor 2006, 36 pp.

ENACON s.r.o. Praha: Studie komplexního řešení kontaminace podzemních vod průsaky z odkališť v oblasti Mydlovary., 2006, 123 pp.

Greenwood N.N., Earnshaw A.: Chemie prvků., český překlad z angl.orig. Chemistry of the Elements., 1984 Pergamon Pres plc., Oxford, 1993, Informatorium, Praha, 1635 pp.

Hanslík E.: Vodní hospodářství 7/1991, 243 p.

Houba J.: Rekultivace a odstranění ekologické zátěže po hydrometalurgickém zpracování uranových rud v oblasti obcí Dívčice, Mydlovary a Olešník regionu BLATA., PBA Group, září 2004, Svazek obcí Blata, 31 pp.

Jež J.: Čas nových uranových dolů ještě přijde., HN 29.1.2007, www.ihned.cz

Jim C.Y.: Ecological and landscape rehabilitation of quarry site in Hong Kong., Restoration Ecology 9 (1), 2001, 85-94 p.

Josefi R., a kol.: Likvidace následků chemické těžby uranu ve Stráži pod Ralskem. In: Sborník XIX. konference Radionuklidy a ionizující záření ve vodním hospodářství, Č.Budějovice, 10.-11.5. 2006, 113-121 p.

Kubátová Z.: Růst cen vrací do hry český uran., HN 25.1.2007, www.ihned.cz/kubatova

Lepka F.: Český uran 1945-2002 Neznámé hospodářské a politické souvislosti., Kosmas.cz, 2003, 102 pp.

Máchová J.: Protokol toxikologického vyšetření povrchové vody., VURH-JU Vodňany, 2006, 5 pp.

Mondspiegel K., Tykva R., Szabool J.: Příspěvek k hodnocení radiační situace v okolí CHÚUP –MAPE Mydlovary., Studie UKE AV ČR, České Budějovice, xx pp.

Pincock, Allen & Holt, 2005: Feasibility Study for the Mydlovary MAPE Remediation Project in Czech Republic., USA, 150 pp.

Reban J.: personal comunication, 2006

Sharmasarkar S., Vance G.F.: Soil and plant selenium at a reclaimed uranium mine., J.of Env. Quality 31(5), 2002, 1516-1521

Tykva R., Švehla J., Škopek P.: (v přípravě do tisku)

Tomášek J.: EIA 2001- Dokumentace o hodnocení vlivu na životní prostředí stavby – Sanace, rekultivace a vyřazování odkališť po uranové činnosti na lokalitě Mydlovary. SOM s.r.o., Mníšek pod Brdy, červen 2001, 260 pp.

Tykva, R., Berg, D.,(Eds.) 2004: Man-Made and Natural Radioaktivity in Environmental Pollution and Radiochronology., Kluwer Acad. Publisher, Dordrecht NL, 416 pp.

Zhu C., Anderson G.M., BurdenD.S.: Natural attenuation reactions at a uranium mill tailings site, western USA. Ground Water 40(1),2002, 5-13p.