

Mine Water Chemistry Development in the R3 Shaft of the Rozna I Uranium Mine, Czech Republic

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ABSTRACT

Keywords:

Mine Water Chemistry Development Rozna Uranium Mine The paper describes the current non-mining state of the Rozna I uranium mine which is located in the central part of the Czech Republic. The subject is a 1 200 m deep R3 shaft which is excavated from the surface. At the R3 shaft is carried out regular monitoring of mine water, specifically inflows to the deposit and their chemistry. Chemical monitoring is carried out by proper collection of mine water and their consequent chemical analysis in an accredited laboratory.

The results of the chemical analysis were processed using standard text and spreadsheet editors and using geochemical modeling software. The paper defines several types of water with slightly different chemistry, but the majority is calcium sulphate type of mine water. Occasional fluctuations in mine water concentrations were not dependent on the concentration of extraction, because at the R3 shaft was extraction of uranium ore terminated in 1996. Fluctuations are attributed only to technological interventions of maintenance work on the shaft. The development of chemistry of mine water was described at the shaft during the years 1994 – 2019. The mine water from the R3 shaft were analyzed for the saturation index. Minerals which could precipitate under specific conditions in the form of amorphous precipitates, coatings or other precipitates, were described.

1. Introduction

Proper management of operating a mining plant among other things consists of regular collection of information from the surface and most importantly from the underground. Because of the issue of mine water, which is pumped from the mine working, tributaries of the deposits are regularly monitored, and their chemical composition analysed. Knowledge of chemistries of mine water in the R3 shaft and other shafts of the deposit is vital for planning the closure of the mine. Based on regular monitoring of the mine water, information about its chemical composition is acquired and over the years an extensive database is thus created. By processing this information, a complex view of the problem is attained and prognoses, how the water will behave in the next years, can be made (Rapantova et al., 2008).

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Mine shaft R3 is the deepest one sinked from the surface in the Rozna deposit (1200,5 m), which makes it pivotal in the future closure of the mine. It will serve as a watery shaft for controlling and monitoring the progress of the mine flooding (Jenk et al., 2009). Also, water for technologies of purification will be pumped through it subsequently and eventually it will serve for monitored draining into the public watercourse.

2. Brief Characteristics of the Area

Uranium deposit Rozna is located in the north-eastern part of Bohemian – Moravian Highland in the Zdar nad Sazavou district, 50 to 60 km to the north- west from Brno, as shown in the figure 1. The spin-off GEAM Dolni Rozinka, which is part of the state enterprise DIAMO in Straz pod Ralskem, carries out permitted mining activities in working district of the area of 8,76 km². The main focus of the mining activities up to 27. April 2017 was underground extraction of the uranium ore (Vokurka, 2018) and its subsequent adaptation into uranium concentrate – ammonium diuranate (NH₄)₂U₂O₇. Nowadays the underground areas of the Rozna I mine are still in operation, they are used by the national organization Radioactive Waste Repository Authority.

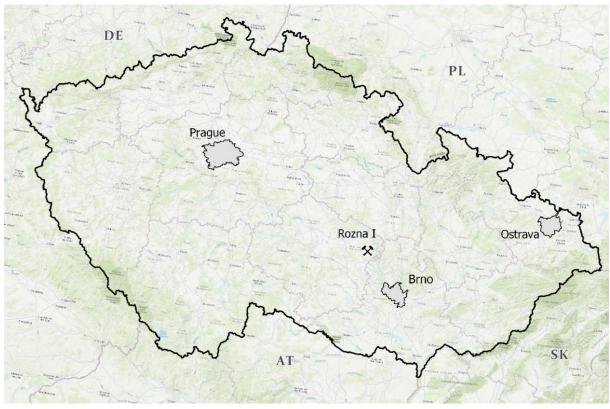


Figure 1. Location of the Rozna I uranium mine in Czech Republic

Based on favourable geological – exploratory results, extraction of the uranium ore in the Bohemian – Moravian Highland began on 27. October 1957. Explorating shafts were taken over from the exploratory group and opening shafts were sinked. On 1. December 1959 began the mine workings in the R2 shaft, the new northern section of the mine. Based on the verification of uranium ore mineralization in this section, sinking of the shaft R3 began in 1962 by enlarging of the exploratory pit n. 27 next to the existing shaft R2. It was designated for mining the northern part under 12th level.

During its lifetime up to the termination of the mining in 2017 the shaft R3 served as a mining shaft for the northern mine areas (Vokurka, 2018). The shaft was the most modern

one in the Rozna deposit and also the only one equipped with a skip bucket. The shaft R3 is 1200,5 m deep which makes it the longest pit driven from the surface in the whole Bohemian – Moravian Highland. 20 levels are carried up from the shaft. Even after the termination of uranium ore mining, the shaft is still kept in working order due to future utilization. After the mine flooding it will serve as a watery shaft for long-term pumping of contaminated mine waters into the purification technologies.

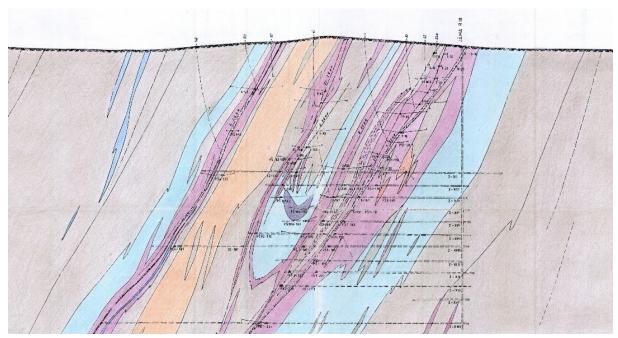


Figure 2. Geological cross-section of the R3 shaft

Source: Vokurka, 2018

Deposit Rozna is a part of ore field Rozna – Olsi, which is located on the north-eastern border of Moldanubian zone. The deposit is located in a complex of meta-igneous sedimentary-effusive rocks from middle Proterozoic age, which was in the late tectonic phases thoroughly complicated by fracture tectonics. Varied group of moldanubians, made up from plagioclase-biotitic to amphibolitic paragneiss of different degrees of migmatization with amphiboles create the rock complex of ground surrounding the Rozna deposit. Marbles, erlan and schist gneiss and small particles of serpentitites and pyroxens are also represented in a small way (Kribek et al., 2008).

Hydrogeological conditions are bound to fissure permeability of the rock massive, which was verified by several exploratory operations during the opening of the deposit and also during the mining. It showed very low transmissivity for the gneiss in the 10^{-9} m².s⁻¹ scale, which increased up to 10^{-6} m².s⁻¹ in the deformation zones. Rocks of the Rozna deposit thus have minimal porous permeability and groundwater of the deep circuit have fissure course dependent on the occurrence of the fissure and dislocation zones (Hähne et al., 2002).

These hydrogeological conditions are confirmed by the tributaries of groundwater found at each individual level. It was discovered, that in the depth of 300 to 500 m under the ground (0-250 meters above sea level) the tributaries are more substantial and indicate deeper groundwater flow, whose direction corresponds with the regional movement of groundwater. Below this level the circulation of groundwater is severely restricted.

The overburden formation of R3 shaft reaches the depth of 1,2 m. These formations follow fine-grained biotite and amphibole-biotitic paragneiss, which reaches the depth of 60 m. Then comes the layer of amphibolite, which is in the depth of 100 m followed by fine-grained biotitic paragneiss. At the 150-200 m level a steep thick tectonic structure (angle of 80°)

divides the layers, it is also a place where significant tributaries are coming into the pit. From the depth of 200 m up to the 12th level amphibolite is found, as shown in the figure 2. At 475 m a 2,5 m thick tectonic rupture (with angle 65°) can be found. From under the 12th level up to the free point, which is 1200 m, the shaft is sinked in coarse-grained biotitic paragneiss, which is affected by various degrees of migmatization, with occasional occurrence of migmatite.

3. Methodology

Mine water is systematically sampled for a complete physical-chemical analysis since 1994 in regular intervals by a worker from spin-off GEAM Dolni Rozinka. Based on availability and usage of the individual levels, the sampling was adapted over the years to best suit the purpose. Sampling was carried out at the measuring points at the 6th level of R2 shaft, which is in the immediate proximity to the R3 shaft and at the measuring points at 12th, 13th, 14th,15th, 16th, 17th, 18th, 19th, 20th, 21th, 22th and 24th level of the pit R3. Measuring points are located at the rill marks in the nearby area of the shaft. At these points devices measuring tributaries coming into the shaft are located, they are a part of the systematic hydrogeological monitoring. Mine water is subsequently analysed in the water laboratory in mill according to the current ISO and EN norms published in Czech Republic as CSN in class 75 (Horakova, 2000). Results are then stored in company's archive.

Data processing was done in MS Excel from 2016, where the data acquired by analytics of mine water were sorted and adjusted. Microsoft Excel is a spreadsheet program by the company Microsoft, which came on the market in 1993 and nowadays is a part of the Microsoft Office suite in each computer with Microsoft OS. Data file was in the end processed by software for geochemical modelling. For the hydro-chemical calculation of saturation index a freeware software PHREEQc was used (Charlton & Parkhurst, 2011), specifically phreeqc.dat, wateq4f.dat database. For the graphic results and interpretation of chemistries of the individual levels a student version of software The Geochemist's Workbench was used (Bethke & Yeakel, 2018).

4. Results

The results are divided into two subchapters, where the trends of monitoring of mine water of floors of the R3 shaft are elaborated in detail. Furthermore, the chemistry of mine waters is described in detail, including minerals with a positive saturation index, which may precipitate in waters under certain condition.

4.1. Trends in Monitoring Mine Water

Concentrations of chlorides in R3 shaft, see fig. 3, have stagnating to growing tendencies with a mild fluctuation since 1994. Lowest figures in range 4,7-8,0 mg.l⁻¹ can be seen at levels 6 and 12 during the years 2001-2009. Highest concentration 87,0 mg.l⁻¹ can be seen at level 6 in 2019. In 1999 a noticeable decrease by 9,9- 14,2 mg.l⁻¹ can be seen at all levels except for 6th and 12th, in 2000 the figures increased by 13,2-19,7 mg.l⁻¹. This fluctuation could have been caused by consequences of heavier precipitation during the years 1997-1998 or by termination of mining in 1995. At the 6th level a rapid increase to 11,005 mg.l⁻¹ can be seen in 2015.

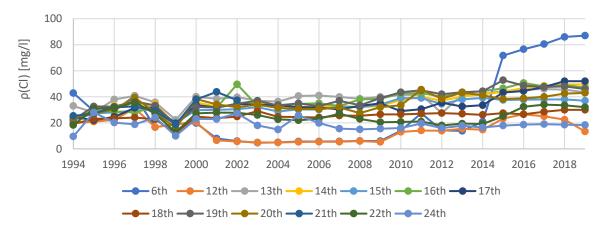


Figure 3. Concentration of chlorides in R3 shaft Source: Vokurka, 2020

Concentrations of hydrogen carbonates in R3 shaft, see fig. 4, have stagnating to decreasing tendencies with a mild fluctuation since 1994 with the exception of 22nd and 24th level, where we can see slowly growing to growing tendency. Lowest number 85,1 mg.l⁻¹ can be seen at level 20 in 2006. Highest number 296,0 mg.l⁻¹ can be seen at level 6 in 1996.

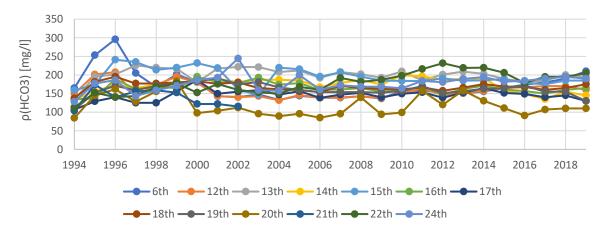


Figure 4. Concentration of hydrogen carbonates in R3 shaft Source: Vokurka, 2020

Concentrations of sulphates in R3 shaft, see fig. 5, illustrate various trends with a substantial fluctuation since 1994. A slight decrease can be seen at level 24, stagnation at levels 6 to 18 and a slight growth at levels 19 to 23. Lowest numbers in range of 68,3-80,7 mg.l⁻¹ can be seen at levels 6 and 12 in 2001-2009. Highest number 2 400,0 mg.l⁻¹ can be seen at level 22 in 2018 and 2019. There is an increase by 825 mg.l⁻¹ at level 22 in 2016.

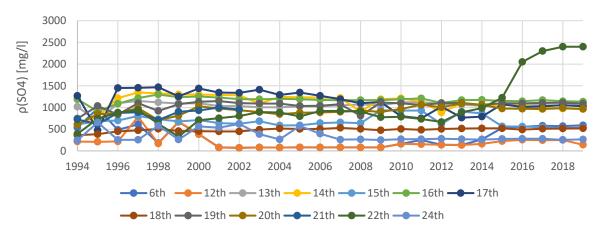


Figure 5. Concentration of sulphates in R3 shaft Source: Vokurka, 2020

Concentration of calcium in R3 shaft, see fig. 6, has mildly growing to growing tendencies since 1994 except for levels 6, 12, 17 and 24, where the numbers are slightly decreasing. Lowest numbers in range of 9.2 - 16.9 mg.l⁻¹ can be seen at level 6 and 12 in 2001-2009. Highest figure 376.0 mg.l⁻¹ can be seen at level 17 in 2003.

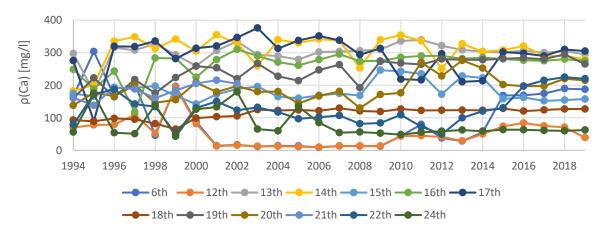


Figure 6. Concentration of calcium in R3 shaft Source: Vokurka, 2020

Concentration of magnesium in R3 shaft, see fig. 7, has a slightly growing tendency with substantial fluctuation since 1994, except for levels 12 and 24 where we can see a slow decrease. Lowest numbers in range 1,4-8,5 mg.l⁻¹ can be seen at levels 6 and 12 in 2001-2009. Highest figure 126,0 mg.l⁻¹ can be seen at level 16 in 2005.

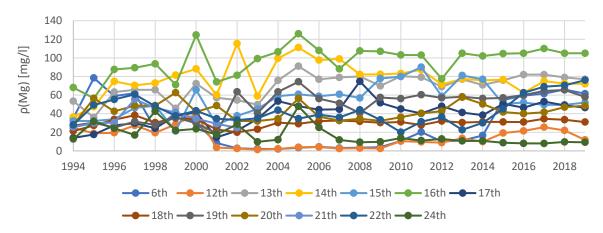


Figure 7. Concentration of magnesium in R3 shaft Source: Vokurka, 2020

Concentration of uranium in R3 shaft, see fig. 8, has a stagnating to mildly decreasing tendency with slight fluctuations since 1994, except for levels 20, 21 and 22, where a mildly growing to growing tendency can be observed. Lowest figures in range 0,009 – 0,016 mg.l⁻¹ can be seen at levels 6 and 12 in years 2001 – 2009. Highest figure 20,600 mg.l⁻¹ can be seen at level 22 in 2007. At 22nd level we can see a substantial fluctuation between 12,050 – 20,600 mg.l⁻¹ during 2003 – 2019, caused probably by purification of the rill marks for better groundwater flow. At level 20 in 2008 we can see an increase by 8,5 mg.l⁻¹ and then a decrease by 8,4 mg.l⁻¹ in 2009.

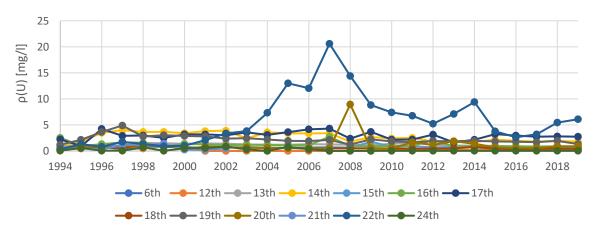


Figure 8. Concentration of uranium in R3 shaft Source: Vokurka, 2020

Concentration of iron in R3 shaft, see fig. 9, has a stagnating to mildly decreasing tendency with slight fluctuations since 1994, except for levels 6, 21 and 22, where a slight increase can be observed. Lowest figure 0,05 mg.l⁻¹ can be seen at level 20 in 2002. Highest figure 36,00 mg.l⁻¹ can be seen at level 14 in 2003. At level 14 and 15 an increase to a range of 31,79 – 35,40 mg.l⁻¹ can be seen in 2003 and then a decrease to 31,74 – 35,92 mg.l⁻¹ in 2004.

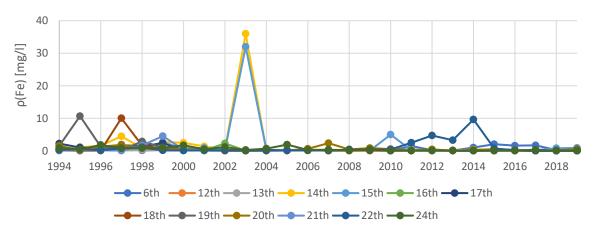


Figure 9. Concentration of iron in R3 shaft

Source: Vokurka, 2020

Concentration of radium in R3 shaft, see fig. 10, has a stagnating to mildly decreasing tendency with slight fluctuations since 1994, except for levels 15, 17, 19 and 22 where a slight to moderate increase can be observed. Lowest numbers in range 23 - 45 Bq.m⁻³ can be seen at levels 6 and 12 in 2001-2009. Highest figure 5 070 Bq.m⁻³ can be seen at level 22 in 2013. At level 22 significant fluctuations in a range 420 – 5 070 Bq.m⁻³ can be seen in 2011-2016, probably due to purification of the rill marks for better mine water flow.

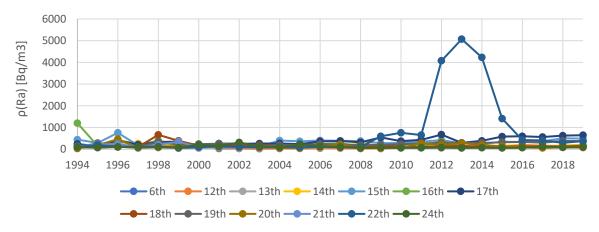


Figure 10. Concentration of radium in R3 shaft

Source: Vokurka, 2020

4.2. Geochemical Characteristics of Mine Water

Three types of mine water can be found in the researched shaft R3, see fig. 11. At most levels, Ca-SO₄ type of mine water can be found. Na-HCO₃-SO₄ type can be found at level 12 and Na-SO₄ at levels 22 and 24.

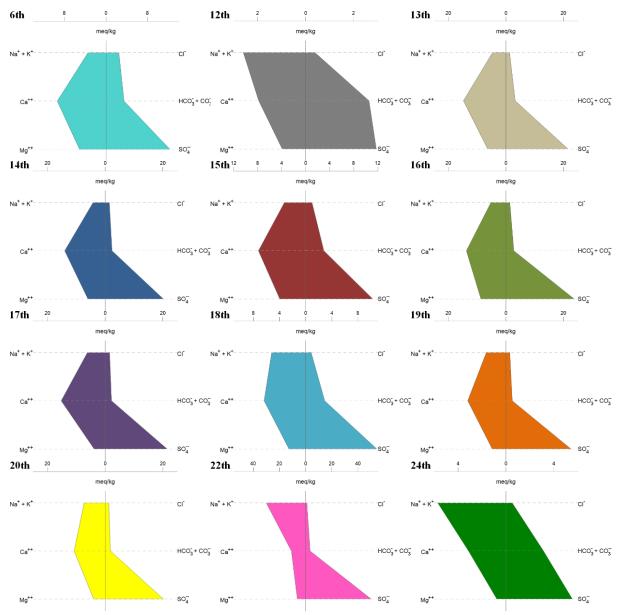


Figure 11. Stiff's diagram of mine water at individual levels, year 2019

For calculating saturation of mine water, chemical analysis, which best represent the whole data file of individual types of mine water, were chosen – levels 6, 12, 18 and 24. Sorted data file was processed by geochemical software PHREEQc, which determined saturation indexes of individual samples. Simulation of saturation indexes for these water phases shows, which materials will be dissolving in the mine area and which will be precipitating. Saturation index 0 shows the state of equilibrium. Although it does not have to lead to precipitation in mine water and if it does, then most likely in amorphous form as leaks, coatings or colloid mixtures.

It is obvious from table 1, that although three types of mine water can be found in the R3 shaft, as far as saturation indexes go, they are very similar. All minerals and their phases, that can precipitate in certain surroundings, are shown in table 1. To a small rate (SI up to 5) aragonite, calcite, dolomite, Fe(OH)_{3(a)}, Fe₃(OH)₈, magnesite and UO_{2(a)} can precipitate. Goethite, haematite, maghemite, magnetite and uraninite_(c), U₃O_{8(c)}, U₄O_{9(c)} can precipitate to a greater rate (SI above 5) (Kvashina et al., 2013).

Table 1.

Minerals showing positive saturation indexes

Phase		6 th level	12th level	18th level	24th level
Aragonite	CaCO ₃	0.93	0.33	0.76	0.63
Calcite	$CaCO_3$	1.08	0.47	0.91	0.77
Dolomite	$CaMg(CO_3)_2$	2.01	0.77	1.54	1.06
$Fe(OH)_{3(a)}$	Fe(OH)₃	2.38	1.33	1.33	1.57
$Fe_3(OH)_8$	$Fe_3(OH)_8$	2.41	-0.74	-0.79	-0.13
Goethite	FeO(OH)	8.27	7.22	7.22	7.46
Hematite	Fe_2O_3	18.55	16.45	16.45	16.93
Maghemite	Fe_2O_3	8.16	6.06	6.06	6.53
Magnesite	$MgCO_3$	0.35	-0.28	0.05	-0.29
Magnetite	Fe_3O_4	18.90	15.75	15.70	16.36
$U_3O_{8(c)}$	U_3O_8	36.74	35.21	36.74	33.23
$U_4O_{9(c)}$	U_4O_9	39.08	37.04	38.91	34.07
$UO_{2(a)}$	UO_2	2.72	2.21	2.66	1.42
Uraninite _(c)	UO_2	7.62	7.11	7.56	6.32

5. Discussion

As far as representation of the main anions, see fig. 12, sulphate ions dominate over hydrogen carbonates in a ratio of $40 - 90 \% \text{ SO}_4^{2-}$ to $10 - 60 \% \text{ HCO}_3^{-}$. Concentration of chloride ions ranges in low figures, up to 15% Cl⁻.

As far as representation of main cations, see fig. 12, calcium ions dominate over magnesium ones in a ratio of 10-70 % Ca^{2+} to 5-40 % Mg^{2+} . Sodium ions are also represented here in a considerable amount 10-90 %, and they are the main cations at levels 12 and 22. Potassium ions concentrations are found only in negligible amounts. The current trend is a slight increase in alkaline ions fraction, mainly Na^+ , which represents up to 90 %.

The whole mineralization, as shown in figure 12, goes in a wide range from 200 mg.l⁻¹ up to 2 400 mg.l⁻¹. pH values of mine water go from neutral to slightly alkaline in between 7,1 and 8,8. A slight increase in pH is apparent, based on the growing concentration of dissolved hydrogen carbonate ions.

Based on a genetics classification, in general, water of R3 shaft can be characterised as mine water, but at certain levels rather as a mixed water. Mixed character of water is due to substantial tributaries of groundwater into the deposit. This can be seen at levels 6 and 12 and in general can be said only about level 12, which is located at the sea level. Under level 12, which means under sea level, there are no substantial tributaries, which means that mixed character of water, such as at level 22, can be attributed more likely to contact with burial or fossil waters.

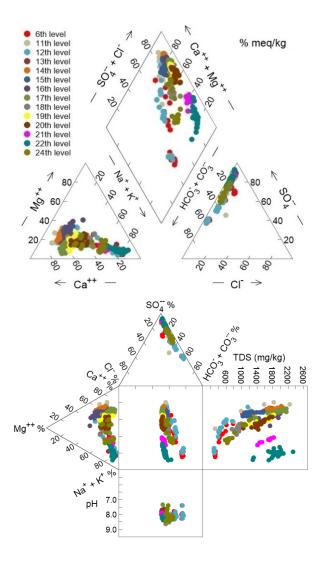


Figure 12. Piper's and Durov's diagram of mine water in R3 shaft from 1994 to 2019

Dynamics of evolution of mine water in R3 shaft in 1994 up to 2019 are strictly dependent on termination of uranium ore extraction, which took place in 1995. Up to that point the concentrations of dissolved elements and its fluctuations depended on the ongoing uranium ore extraction. After 1995 a fast decrease of activity in the shaft can be seen, including the movement of people. The total concentration of mine water is in high amounts, but after the termination of extraction of the uranium ore and slow abandonment of this area, the values are slightly decreasing.

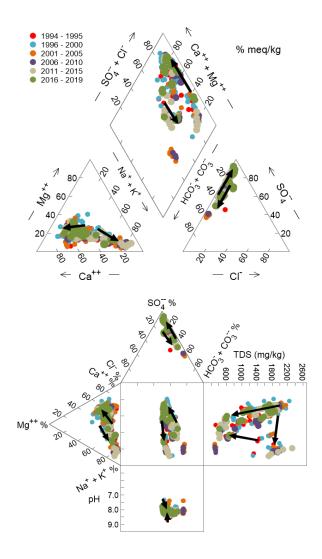


Figure 13. Piper's and Durov's diagram for evolution of mine water in R3 shaft in time

The mine water character is mostly sulphate during the whole observed period of 1994-2019. However, there are slight decreases and increases in ratio of sulphates as the main anions and the main cations. An important trend is an increase in alkaline metals, mostly sodium ions, as shown in figure 13. Furthermore, prevailing representation of calcium ions over potassium ones is obvious.

6. Conclusions

Uranium ore was extracted for almost 60 years at the mine Rozna I with the greatest boom in the 1960s and 1970s. By establishing the attenuation programme in the beginning of 1990s the uranium mine extracting was limited only to mine Rozna I. Concentration of chemistries in mine water was dependent on the course of extracting of the uranium ore, but the extracting was terminated in 1996 in the R3 shaft. Since then the occasional fluctuations in trends of chemistries in mine water can be explained by technological maintenance of the mine in most cases. Also, some natural causes can have a say, such as increased amount of precipitation.

Character of mine water in R3 shaft can be described as mine water with preponderance of sulphate and calcium ions. With increasing depth, the calcium cations are substituted with sodium cations and in the deepest parts of the deposit the sulphate anions are substituted by hydrogen carbonate anions. Then the mine water's characteristics change into waters of the

deep circuit. Based on monitoring of the evolution of the last 20 years it can be said, that mine water in the R3 shaft is distributed into three layers with varied chemistries based on increasing depth. At levels 1 - 20 a Ca-SO₄ layer can be found, with the exception of Na-HCO₃-SO₄ layer at level 12. Na-SO₄ layer is at levels 22 - 24. Varied character of mine water is most likely due to substantial tributaries into the deposit or by contact with burial or fossil waters.

Precipitates can form under certain conditions from these types of mine water, in forms of leaks or amorphous coatings. 14 minerals or their phases can be created, 4 of which contain uranium element.

Acknowledgments

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