Simulation of solubility and equilibration rate of relevant coal seam: a stable isotope and chemical study

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ABSTRACT

The problem of water irruption into coal mines (Ojstro and Hrastnik, Slovenia) is discussed from a geochemical point of view. Laboratory simulations of solubility rate, chemical equilibration and isotope fractionation are the goal of the current research. 30 day experiments have been carried out for all the important constituents of the coal seam. The experimental range of $\Delta\delta^{13}C$ in HCO_3^- (DIC) attained 14 ‰ (-14.8 to –0.8‰) and $\Delta\delta^{13}C$ in a single experiment can exceed 8 ‰. Carbonate rocks (limestones, dolomites, marls) have $\delta^{13}C$ from -6 to +3 ‰ and $\delta^{13}C$ of coal is between –23.7 and –20.6 ‰. The experimentally observed sulphur isotope composition varies from -13 to +17 ‰, whereas the $\delta^{34}S$ of sulphur minerals is –23.7 to +38.4 ‰, indicating sources from sulphides and initial sulphates. Both isotope characteristics are evidently selective for the mine materials tested. Chemical examination of selected mine samples equilibrated with Ca^{++} and Mg^{++} hydrogen carbonate water showed that sulphate and sodium compounds are dissolved quickly, while the hydrogen carbonate dilution rate is slower. The exception is coal, which intensively adsorbs calcium and magnesium from the water solution. The end point characteristics of a particular aquifer composition at ambient temperatures were attained within a period of days to several months.

Key words: coal, mining, Slovenia, mine waters, isotopes, carbon, sulphur, isotope fractionation, ion exchange, solubility rate.

INTRODUCTION

The risks of water irruptions into the brown coal mines of the Zasavje mining region are very serious. Therefore the water sources and water percolation through the coal seam has to be studied from geochemical point of view. The Ojstro and Hrastnik mines have been investigated. The bedrock of the coal seam consists of Triassic dolomite mostly overlain with marls and grey clays of Oligocene age. The coal seam was formed in very shallow brackish basins and is overlain with marls, silicate sandstone and lithothamnian limestone.

We were interested mainly in those of the hydrogeological processes that alter the isotope composition of water and dissolved matter, as well as the chemical composition of water, which can be used to determine the origin and the movement of ground water. For the exact determination of the origin of the mine water in mine workings and to determine the characteristics of aquifers and the accumulations in which water may be retained multicomponent approach is necessary. For tracing its movement from the surface to individual inflows in mine workings, complex isotopic and geochemical analyses of mine water are needed.

The isotope composition of oxygen and hydrogen in ground water match closely the isotopic composition of meteoric water. The values of $\delta^{18}O$ and δD as well as the concentration of tritium in rainfall and in surface waters in the investigated territory change with time within the course of a year. This is a result of seasonal isotope variations ($\delta^{18}O$ during winter is around -12 ‰ and during summer time values reach –5 ‰). Ground water is isotopically quite homogenised. In the Zagorje mines $\delta^{18}O$ varies from –10.6 to –9.6 ‰ and δD from –77.2 to –69.3 ‰ (Dolenec et all., 1989). In spite of a relatively high degree of isotope homogenisation in the aquifers and accumulations it is still possible to estimate the time required for these waters to appear as mine waters. This can take anytime from one month to several decades. On the basis of tritium measurements the age of mine waters is usually less than ten years, however, certain waters date back to before the first atom bomb tests - approximately 40 years, when tritium concentrations in the atmosphere were as low as 10 T.U. The latter values increased to several 1000 T.U. due to atmospheric testing (Faure, 1977, Hoefs, 1987).

Mass spectrometric analysis revealed that the $\delta^{13}C$ in dissolved carbonate from the Ojstro mine is between –12.5 to +1.1 ‰ and is similar to the isotope composition of the dissolved carbonate from the Hrastnik mine (-15.9 to –9.8 ‰). In the Hrastnik mine the main aquifer is the fractured hanging wall marl which is separated from the lithothamnian limestone by a marine grey clay (Galimov, 1980). The isotope data may reflect the extensive rockfall processes triggered by the intensive mining of coal from the upper part of the stage that resulted in wide water bearing fissures. These cut the hanging wall marl, which is several meters thick, and reach across about 50 m of sea clay into the lithothamnian limestone.

The $\delta^{34}S$ of sulphur bearing compounds in mine varies between –23.7 and +38.4 ‰, consequently is 62.1 ‰. This enrichment with the heavy sulphur isotope is quite unusual. The major enrichment of sulphate sulphur with the heavy isotope and the most extreme oscillations in sulphate concentration were found in the mine water from certain active stopes and old workings. Sulphates enriched with the light sulphur were also detected, which means that total oxidation of biogenic sulphides takes place in particular places - mainly in old galleries (Dolenec et all., 1987).

METHODOLOGY

The laboratory simulations of solubility, chemical equilibrium and isotope fractionation in the coal mine Ojstro (Slovenia) were the goal of this research. Tertiary limestones, Triassic dolomite, overlying marls, Oligocene grey marine clays, kaolinite inclusions and coal have been selected from relevant lithological as well as petrological units. Coarse grained particles (2 - 5 cm) have been equilibrated at 200°C using the Ca/Mg hydrogen carbonate water from the same mine as the control. 7 to 12 kg of prepared material was placed into a 25 liter glass vessel and the remaining volume filled with the control water. The Vessels were then tightly sealed to prevent gas exchange and water evaporation. The stable isotopes (carbon and sulphur) and chemical species concentrations (Ca^{++}, Mg^{++}, Na^{+}, K^{+}, Cl^{-}, HCO_3^{-} and $SO_4^{=}$) in the water solution were measured 4 or 5 times during a period of one month. The first sample was taken as the zero point - start of experiment with initial water. A second sample was then taken after 7 days, a third after 14 days and the last after one month. Several analyses were also made after the second month. In addition, the mine waters, rocks samples, minerals and coal were isotopically and chemically examined.

Isotope analyses were made using mass spectrometry (Varian MAT and MS-7) with a precision of ±0.1 ‰ for oxygen and carbon, ±0.2 ‰ for sulphur and ±0.5 ‰ for hydrogen. Spectroscopic and liquid chromatographic techniques were used for the chemical analytic.

RESULTS AND DISCUSSION

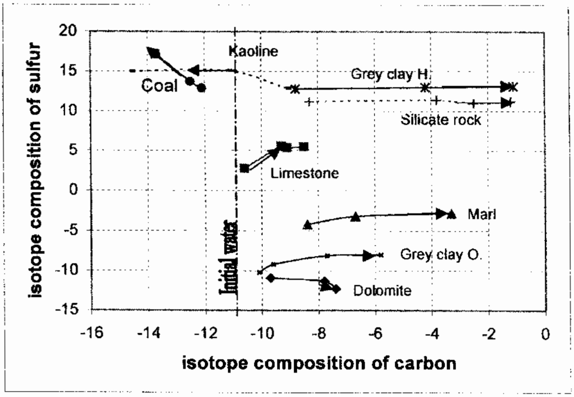

Figure 1: Correlation of isotope composition of carbon vs. sulphur attained during exchange experiments for different natural materials from two brown coal mines: Ojstro, Hrastnik. The arrows indicate the direction of progress of isotope fractionation during a period of one month.

The isotope composition of carbon in dissolved carbonates (DIC) and sulphur in dissolved sulphate species was determined in the foot wall dolomite, hanging wall lithothamnian limestone, grey marine clay, kaolinite lenses, hanging wall marls, silicate sandstone, and in brown coal rich in sulphur compounds (Figure 1).

The range of $\Delta\delta^{13}C$ in HCO_3^- (DIC) exceeds14 ‰ (-14.8 to –0.8 ‰) and $\Delta\delta^{13}C$ in a single experiment can exceed 8 ‰. According to $\delta^{13}C$ all samples, except for kaolinite and coal show an isotope exchange with carbonates ($\delta^{13}C$ from -6 to +3 ‰). Taking into account that these experiments lasted no more then one month, the results suggest that compact limestones and dolomite exchange more slowly than carbonate bearing marls and grey marine clays rich in silicate minerals. This is especially true for sandstone, which is practically free of carbonates. Also clays from different mines (Ojstro and Hrastnik) appear to react quite differently.

The dissolved sulphur isotope composition determined under experimental conditions is broader than that of carbon. These observed variations range from -13 to +17 ‰. From dolomite the negative $\delta^{34}S$ is washed out in quite low concentrations. A similar concentration range is also washed from limestone, albeit the $\delta^{34}S$ values are more positive. The Analyses of the clay samples suggest that the two mines were formed in different environment and underwent different diagenic processes. Namely, in Ojstro sulphate with constant values around -4 ‰ are washed from clay, while in Hrastnik the range around +13 ‰ is found. The mineralogy of the clays is still to be studied in detail. Coal is the only environment where the $\delta^{34}S$ shifts significantly in a positive direction, and has the most positive values among mine materials tested. The reason for this may be the equilibrium oxidation of sulphides and organic sulphur in the samples (strata), where as a result of isotope fractionation ($S^- : S^{6+}(SO_4^=)$) very positive $\delta^{34}S$ are present in sulphates (Robinson, 1987, Krouse, 1988).

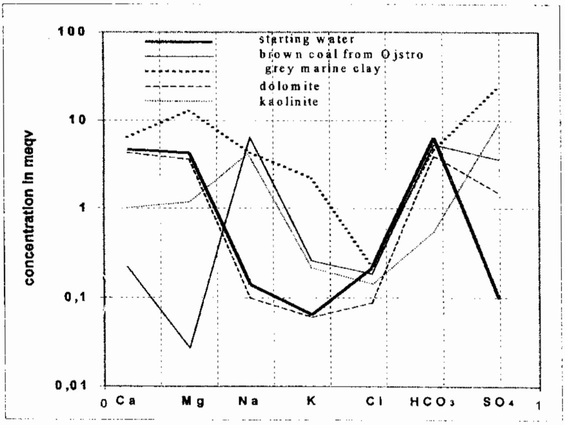

Figure 2: Final water chemical composition after one month exchanges of coal mine rocks material with initial water (bold line). Calcium, magnesium, sodium, and sulphate species are the most active (modified Schoelle's diagram)

In general carbon species are exchanged more intensively during a period of one month, while sulphur isotopes are characteristic for an individual environment, but remain fairly constant in one milieu.

The main characteristics of the chemical part of the laboratory simulations are shown in Figures 2 and 3. The most important is the initial water at the experiment starting day_(bold in Figure 2 and starting time point in Figure 3). Equilibration with brown coal, grey marine clay, dolomite and kaolinite lenses were carried out. The final waters are depleted with Ca^{++} and Mg^{++} in dolomite, kaolinite and especially in coal but are enriched in the case of clay. Sodium and potassium are enriched while chlorine is slightly depleted. Hydrogen carbonate species are a slightly depleted compared to the initial water values with the exception of kaolinite, which is significantly depleted. Also significant is the high concentration of sulphate ions ($SO_4^{=}$), where the sulphate concentration in clay reaches a maximum value greater than 20 meqv after 30 days.

The rate of re-equilibration of the initial water with dolomite, grey marine clay and coal is discussed according to data in Figure 3. In dolomite slight changes in all chosen species (Ca^{++}, Mg^{++}, Na^{+}), except for sulphate ($SO_4^{=}$), are observed. Clay is characterised by the most intensive and abundant solubility of all the discussed species. The most unexpected exchanges were found for the tested coals. Initial amounts of Ca^{++} and Mg^{++} are quickly adsorbed (by a factor of 30) followed by an increase in the concentration Ca^{++} in the solution, while Mg^{++} is almost completely removed (0.01 meqv). Sodium remained low, hydrogen carbonate changes only slightly from its initial value, while the sulphate species reach values significantly lower than those of clay.

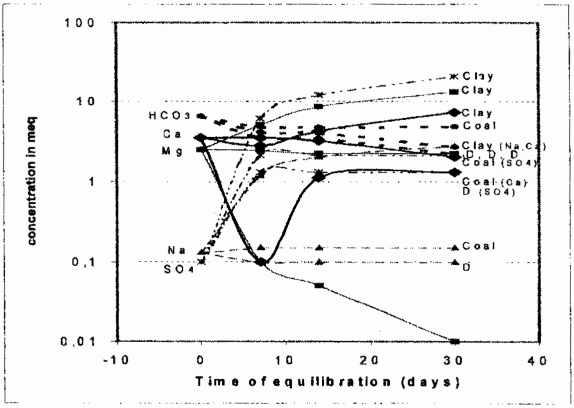

Figure 3: Exchange progress (solubility rate) between mine rock material and initial water during a period of one month. Dolomite, clay and coal were tested. The exchange reactions can be followed for individual species. The main part of equilibration is complete within the first seven days.

In general HCO_3^- shows a trend of moderate depletion during the experiments in all the examined samples. Of all the processes studied the exchange reactions and washing of Ca^{++} and Mg^{++} appear to be the most complex. The equilibration direction is changed with time and end points, compared to initial water, are extreme. It is evident that for dolomite and coal the solubility and washing out of sulphate is rapid and almost complete within the first 7 days, while for clay the concentration of sulphate doubles over the next 20 days.

CONCLUSIONS

By testing the different lithological and petrological units in the coal mines Ojstro and Hrastnik (Slovenia) under static laboratory conditions it was found that in a particular environment the results of chemical exchange and isotope fractionation can give useful data for detecting sources of water irruptions into the mine galleries.

- In all the samples the similar range of $\delta^{13}C$ values (-14.8 to –0.8 ‰) was found. But marls and clays contain a lot of soluble carbonate components, which result in a $\delta^{13}C$ value of nearly zero (0), characteristic for carbonates. Water in equilibrium with dolomite and limestone show $\delta^{13}C$ values of approximately –8 ‰, while coal and kaolinite aquifers can be represented by values of –14 ‰.
- Measured $\delta^{34}S$ values indicate that a particular reservoir is homogeneous, but the range of values between reservoirs is large (-13 to +17 ‰), suggesting that the source of the constituents and the production of soluble species ($SO_4^=$) are different. Regarding to the water recharge from different aquifers into the mine galleries it is convenient to use the sulphate isotope data. The data can be very useful especially in correlation with $\delta^{13}C$.
- It was found from laboratory experiments using different rock units that a particular aquifer can be characterised by its chemical composition. In the examined water-rock exchange experiments the most selective are Ca^{++}, Mg^{++} and Na^+ as cations and $SO_4^=$ as anion.
- The examined clay, dolomite and coal samples show that sulphate is exchanged very quickly, while HCO_3^- a good buffering system, changed slowly. Surprising is the almost total adsorption of Ca^{++} and Mg^{++} from water to coal. Nevertheless, the end point characteristics of a particular aquifer composition can be achieved over a time period ranging from days to months.
- The rate of solubility and isotope exchange is variable and in real samples not only express the solubility rate but also the diffusion from the inner part of the examined material, but more important is the total concentration exchange in time unit.
- In mine waters it is customary that waters are mixing, although, they do not always attain equilibrium. However, the main characteristics remain, as established through our investigations of mine water and minerals (including coal).

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