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ORIGIN OF NITROGEN COMPOUNDS IN WATER INFILTRATING INTO PORPHYRY QUARRY, ZALAS, SOUTHERN POLAND.

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ABSTRACT

The paper deals with the problem of the origin of nitric compounds in the mine water entering porphyry quarry. A hydrogeological study of the natural and disturbed ground water regimes as a consequence of quarrying have shown that fecal and domestic sewage was the main source of nitrogen compounds in the water entering the porphyry quarry.

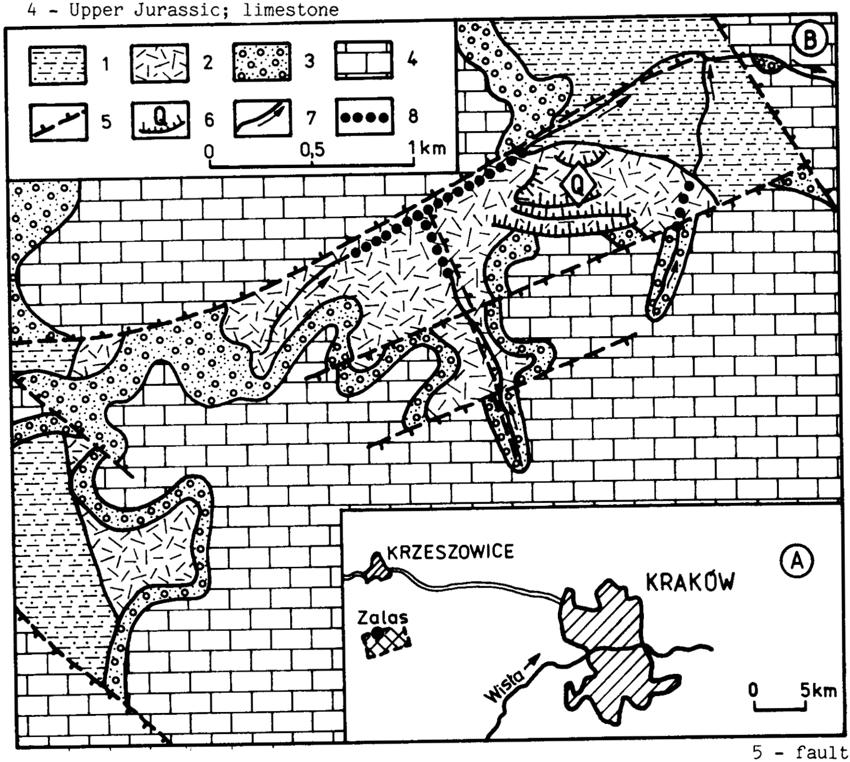
The sewage contaminated the surface water which in turn infiltrated into the porphyry within the cone of depression. In addition to that, NH_4^+ and NO_3^- ions penetrated into the surface water as the result of washing of nitrogen out of the soil and as a product of biochemical and chemical changes in the soil.

A solution of unburnt explosives, used for the ground excavation was also a source of nitrogen compounds.

INTRODUCTION

The paper considers the origin of nitrogen compounds in mine waters in a porphyry quarry in Zalas, near Krzeszowice - about 15 km to the west of Cracow (Figure 1a). The present quarrying operations of porphyry are being carried out below the natural level of ground water. The disturbance of the original water regime in the region of the deposit created a number of new problems. One of them was the quality of mine waters discharged into one of the streams passing by. As a result of observations lasting for several years, it was concluded that the waters discharged from the quarry complied with the appropriate environmental requirements clarily but the concentration of NH_4^+ and NO_3^- ions were too high. The authors of this paper attempt to explain whether the nitrogen compounds contaminating ground water was a result of the mining activity or otherwise.

1 - shales and sandstones; Permian
2 - porphyry; Jurassic
3 - Middle Jurassic sands, sandstones
4 - Upper Jurassic; limestone



5 - faults
6 - the quarry
7 - streams
8 - dry stream beds.

Figure 1 (a) The site map of the investigated area
(b) The geologic map of the area

THE GEOLOGICAL SETTING AND HYDROGEOLOGY OF THE REGION OF THE QUARRY IN ZALAS

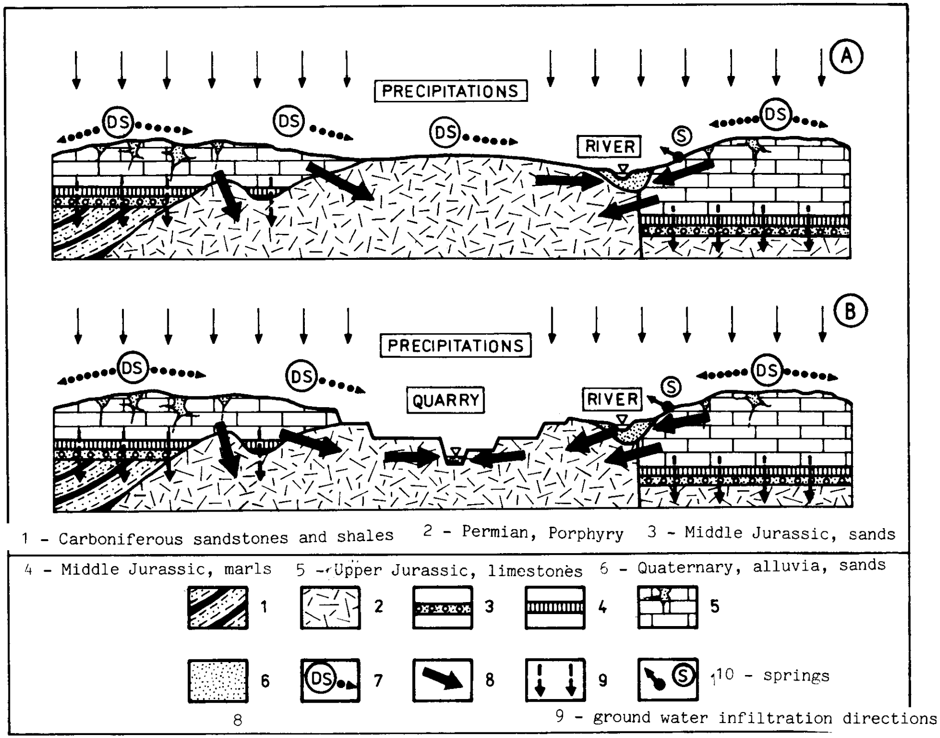
Carboniferous sediments are the oldest outcropping rocks on the surface and consist of Lower Carboniferous shales with limestone and sandstone as well as of shales and sandstones of the upper carboniferous period. Extensive porphyry laccolith had formed in the region of Zalas in the Permian period and it intruded between the strata of the Lower and Upper Carboniferous period. The porphyry is exploited in the quarry in Zalas. Between the Permian and Middle Jurassic periods intensive processes of erosion took place in the area. It resulted in an outcrop of the upper part of Zalas laccolith (Bogacz, et al, 1984). Middle and Upper Jurassic formations lie unconformitely on Carboniferous rocks and on porphyry. The Middle Jurassic period is represented by a 10 m thick series of sands and sandstones, which become sandy limestone in the roof parts. The rocky limestone and 10 m thick series of marls and limestone bedded in the floor date from the Upper Jurassic period. Quaternary sediments mainly of post glacier origin are the youngest formations found in the area; appearing in the morphological pits of older geological formation, forming moraine clays, fluvioglacial sands, loesses and loess-like clays. Four aquifers can be identified in the area namely the Quaternary, Jurassic, Permian and Carboniferous (Figure 1a). The Quaternary aquifer consists of Pleistocene formations, mainly of sands and gravels which fill buried river valleys (Dzukynski, et al, 1966). The propagation of the aquifer is rather limited, but it may be important for the water circulation because of its great thickness (up to 100 m).

Two horizons, Middle Jurassic and Upper Jurassic, can be distinguished within the Jurassic aquifer. The Middle Jurassic horizon consists of a sand-gravel and sandstone-limestone formation. It is a pore or fissure - pore horizon of a rather small range of permeability and storage coefficient Rocky and in some places bedded limestones constitute the Upper Jurassic aquifer. It is a typical karst-fissure reservoir of ground water with high anisotropy of hydrogeological qualities. This heterogeneity is connected with the level of fissuration and karstification of limestones. The Upper Jurassic aquifer is isolated from the floor by pockets of Cordata marls.

The Zalas porphyry is a typically fissured aquifer in which the water circulates along a system of fissures of various origins and the Permian water-bearing reservoir. In this region the thermal (Dzulynski, 1953), tectonic and weathered (Bogacz, et al, 1984) and fractured rock can be distinguished. The complicated system of fissures is present in different regions with different intensity and that is why the reservoir is very heterogenous.

The upper one is intersected by a compact net of thermal (circumferential joint) and exogamic fissures. The lower one is intersected with conical and radiant joints and a far rarer net of fissures. The present exploitation levels of the quarry occur in the upper zone of porphyry which is characterized by higher permeability and storage coefficient. The carboniferous aquifer is a typical horizon consisting of several beds of sandstone banks separated from roof and floor by impermeable shales. The carboniferous aquifer is directly exposed in the surface mining excavation at Zalas.

The aquifers in the region of Zalas are hydraulicaly connected with one another in various contacts zones (Figure 2). The natural primary



1 - Carboniferous sandstones and shales 2 - Permian, Porphyry 3 - Middle Jurassic, sands

4 - Middle Jurassic, marls 5 - Upper Jurassic, limestones 6 - Quaternary, alluvia, sands

10 - springs

8

9 - ground water infiltration directions

Figure 2 The simplified diagram of the ground water circulation in the region of Zalas under natural (A), and under disturbed regime (B) sedimentary-transgressive and secondary, tectonic type contacts have the most important role of all. The conditions of underground water circulation in the region of Zalas are very complex. When the porphyry was not exploited or when it was bailed out above the level of ground water in intrusion, there were primary conditions of circulation, ie from the natural regions of recharge to the natural zones of drainage.

Streams as well as a few springs of little yield were natural local sources of the drainage (Figure 2). Under these conditions, the Permian water-bearing floor was supplied by at least two sources:

- the infiltration of precipitation on outcrop of porphyries,
- by the flow of underground water, in the zones of hydraulic contacts, from the Jurassic aquifer to porphyries or through aquifer infiltration of waters from the Upper Jurassic through Cordata marls and through the Middle Jurassic horizon.

Probably the Permian porphyry was also recharged by a magma intrusion from the Carboniferous aquifer (Figure 2). After the exploitation of porphyry below the water level had started, the directions of the flow changed. The direction of the water flow from the Jurassic aquifer to porphyry laccolith through the spheres of hydraulic contacts and Cordata marls was preserved. However, the directions of the underground water flow in the vicinity of stream valleys underwent inversion (Figure 2).

The water from the surface water-courses together with the domestic sewage released from the surrounding villages started to infiltrate the porphyry foundation. They preserved their drainage character only on these sections where the waters flow on Jurassic sediments. Nowadays a complete disappearance of streams and domestic sewage, carried away from farmsteads by ditches, is observable in some sections (Figure 1). There are also observable shortfall of water in springs and domestic wells sunk in the porphyry aquifers. In the zones of hydraulic contacts between Permian and Carboniferous aquifers, the ground water regime is disturbed causing a flow from the Carboniferous formations to the porphyry.

In summary, water from the following sources emanate in the quarry in Zalas:

- water of the precipitation falling directly into the quarry,
- precipitation waters flowing into the pit from the slopes of the Jurassic hills surrounding the open pit excavation from the North and the South-West,
- precipitation water percolating through the zone of aeration on the porphyry - outcrop region,
- stream waters and domestic sewage infiltrating the porphyry,
- water from static resources incorporated in the porphyries,
- water flowing from the Jurassic aquifer through the zones of hydraulic contacts and percolating through Cardata marls,
- waters flowing into the quarry along a complicated way, eg from Jurassic aquifer to the Carboniferous sediments and then to porphyry.

ORIGIN OF NITROGEN COMPOUNDS IN SURFACE AND UNDERGROUND WATERS

There may be a number of sources of nitrogen compounds in underground and surface water in the region of Zalas as follows:-

(i) fertilization by mineral and natural fertilizers containing nitrogen compounds,

(ii) natural biochemical processes taking place during the decay of the soil organic matter, O- fecal and domestic sewage, and

(iii) chemical processes connected with the use of ammonium nitrate for blasting in the Zalas quarry.

The possibility of washing out of the soil the ingredients of the fertilizer and accordingly resulting pollution of the ground and surface water is one of the short comings of both natural and mineral fertilization. The loss of nitrogen from the soil by rains depends strongly on the dosage of the nitrogen fertilizer, amount of precipitation, kind of soil, and first of all on its nitrogen abundance and the plant types (Gerlach, 1979). The greatest washing of nitrogen on cultivable soils takes place in winter, ie between the periods of plant vegetation.

Most of the area under investigation lies within the range of cone of depression caused by the porphyry quarry in Zalas on arable land. Only the surrounding valleys of some streams are used as meadows. This fact allows for a presumption that fertilization of arable lands by nitrogen fertilizers contributes to the pollution of ground and surface waters by ammonium nitrogen.

Not all of the scientists concerned with environment pollution caused by nitrogen are ready to link this phenomenon solely with the fertilization with nitrogen rich fertilizers.

Some of them maintain that density of population and housing of animals have the greatest influence on the amount of nitrogen in the water. Analogically, Bernhard, et al (1969) during their investigation found the greatest amount of nitrogen on an area of great population, through arable lands represented a considerably small part of the region when compared with grassland.

There are three villages in the vicinity of the quarry in Zalas, which surround it by an almost compact settlement along the roads. Most of the inhabitants have farms and run stock and swine farming. The villages mentioned above are not sewered. In spite of the fact that most of the domestic and fecal sewage is carried away to fecal tanks a significant load of pollution penetrates into the ground water through the tanks. This has been found on the basis of previous experiments carried out by the authors as well as on the basis of examining the great concrete tanks. The contamination gets through the leaky tanks and also directly from uncased containers of liquid manure and after being washed by precipitation waters from the surface of the ground may supply a significant load of nitrogen compounds, especially in case of dense settlement in the region of the quarry. The contamination will consist mainly of the ammonium nitrate.

The fact that ammonium nitrate is delivered by the fecal and domestic sewage may be high was proved by Koc (1979) who estimated that the liquid

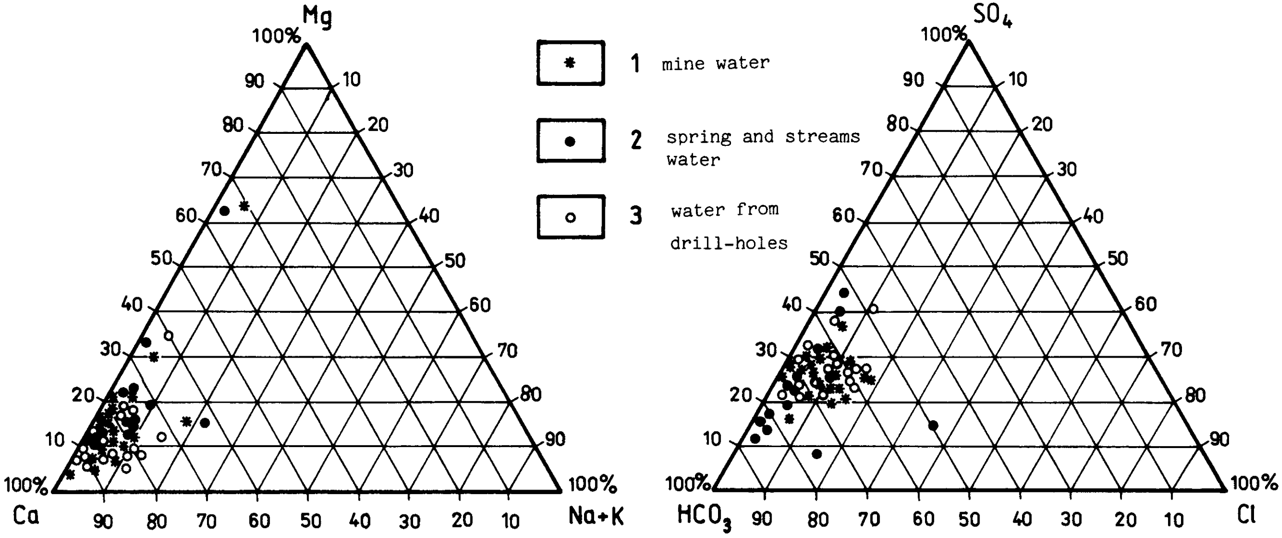


Figure 3 The chemical constitution of water from the region of Zalas

manure contains from 247 to 2880 mg/dm³ of NH_4^+.

The quarry in Zalas receives almost all the surface water which flows through most of the mentioned villages. It drains the water of the first water level in their area as well. Ammonium nitrate used in the quarry in the process of blasting may be another source of ammonium nitrate in mine water. Using this ingredient of explosives may cause the ammonium nitrate to infiltrate into the ground water as the result of the following processes.

(a) Blasting in holes covered with water. Ammonium nitrogen is highly hydroscopic and readily soluble. That is why inaccurate blowing through of the blast holes and leaving some water in them before loading of ammonium nitrate may help getting the NH_4^+ ions into ground waters.

(b) The same process may take place after loading the blast-hole with the explosive.

(c) Incomplete combustion of ammonium nitrate at the moment of explosion.

(d) Passing of firing gases, along various ways, into ground water, the gases apart from CO_2, H_2O, O_2 and N_2 consist of: N_2O, NO, NO_2, and NH_3.

RESULTS OF THE INVESTIGATION OF SURFACE AND GROUND WATER CHEMICAL CONSTITUTION IN THE REGION OF ZALAS

Out of the total of 50 samples, 20 were taken directly from the quarry (outflows or stagnating waters in the about 290 m level above the sea level), 8 samples were taken from bore holes (blast, piezometers and (hydrogeological), 18 from surface water-sources in the region of the porphyry mine in Zalas and finally 4 samples were taken from wells.

Figure 3 show the synthetic results of the investigation of the chemical composition. The water flowing into the quarry are fresh waters. Their mineralization equals from 365 to 537 mg/dm³, and average of 417 mg/dm³. The concentration of ammonia nitrogen (NH_4^+) was certified to amount from 0.0 to 3.0 mg/dm³, the average of 1.51 mg/dm³. The concentration of nitrate nitrogen in the mine waters amounted from 2.5 to 12.0 mg/dm³, the average of 6.48 mg/dm³. The concentration of the other chemical compounds in the waters did not exceed either the Polish standards for drinking water or the standards established for the surface water of the first class of clarity.

The mineralization of the surface water courses stays within the limits between 372 and 673 mg/dm³, tne average being 451 mg/dm³. They are fresh waters of HCO_3 - Ca chemical type, and sometimes of the type HCO_3 - So_4 - Ca. In comparison with water flowing out of the quarry this water has a characteristically higher concentration of ammonium nitrogen, ie from 0.5 to 4.0 mg/dm³ average 1.92 mg/dm³. On the other hand the concentration of NO_3^- ion are lower.

The waters taken from the drill-hole have characteristically lower mineralization in comparison with surface water. Similarly to surface waters it has chemical type HCO_3-Ca or HCO_3-SO_4-Ca. Its mineralization oscillates within the limits of 272 to 338 mg/dm³, the average of 314 mg/dm³. The concentration of NH_4^+ and NO_3^- ions is also lower in comparison with the water mentioned above. Their average concentrations equal accordingly 1.19 and 4.38 mg/dm³.

On one hand, it is justified by the fact that they contain more precipitation water infiltrating directly through fissured rock mass when compared with surface water and the water pumped from the mine (Figure 2). All the holes, from which the samples were taken, were situated where precipitation waters may infiltrate directly into porphyry. The precipitation water has low mineralization: the minerals which compose porphyry, on the other hand, are hardly soluble. Also the changes of nitrogen compounds which take place in the surface water and the shallow ground water, from the reduced forms (HN_4^+) to oxidized forms (NO_2^-) and NO_3^- under conditions of good oxygenating of the water, cause the lower concentrations of NH_4^+ and higher of NO_3^-.

The result of the changes may be reduced in fact to the decrease of ammonium nitrate and increase of nitrate nitrogen concentrations. This is obvious when the concentrations of NH_4^+ in the surface water and that one, certified in drill-holes water is compared. The average concentrations of ammonium nitrogen in the mine water certified during the investigation, which equal 1.51 mg/dm³, are higher in drill-holes which were placed in the direct vicinity of the working of the lower exploitation level. This would indicate the fact of enriching the waters flowing into the quarry with the ion, probably during the blasting activities. The results of the test of mine water taken from the longwall directly before and just after the blasting, are ambiguous. In one series of measurements the concentrations of NH_4 were higher after blasting than before it. In another series the concentrations of NH_4 before and after the blasting were the same.

Realizing certain limits of inference on the basis of the arithmetical average, the authors were inclined to state that the mining activity of the quarry influenced the increases of the amount of NH_4 ion in the quarry water. It can be claimed on the basis of the average concentrations of NH_4, that the ammonium nitrate content in the mine water discharge is in proportion to that in the water inflow into the mine. It equals about 0.32 mg/dm³, ie 20% of the average contents in mine water. The water which stagnates or which has a very slow flow in No 3 level becomes oxygenated and change into NH_4-NO_2-NO_3 type compound.

CONCLUSIONS

After the exploitation of porphyry below the natural ground water level, water of high nitrogen compounds contents started to flow into the quarry. During the investigation period the average concentration of NH_4^+ ion in the water equalled 1.5 mg/dm³. Surface water, which infiltrates into the porphyry in the region of the cone of depression is the main source of nitrogen compounds in the mine water. It contained on average 1.9 mg/dm³ of NH_4^+ ion and 4.3 mg/dm³ of NO_3^- ion. About 0.3 mg/dm³ of NH_4^+ ion, ie about 20% originates from the washing of the unburnt blasting material from the blasting holes.

The pollution of surface water by nitric compounds may be attributed to fecal and domestic sewage from the farm buildings and fertilization of cultivable lands. Natural biochemical and chemical processes and changes in the aeration zone may also be a source of nitrogen compounds. The process occurs during the infiltration of the precipitation water to the saturation zone.

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