POLSKIE TOWARZYSTWO MINERALOGICZNE – PRACE SPECJALNE
MINERALOGICAL SOCIETY OF POLAND – SPECIAL PAPERS
Zeszyt 22, 2003; Volume 22, 2003

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ACTINIDES AND HEAVY METALS IN CLAYEY ROCKS OF POLAND – SOME EXAMPLES

INTRODUCTION

The problem of trace elements in clayey rocks of Poland is the subject of many papers, both of a basic character and the applied ones. In the process of chemical weathering under the influence of different factors on parent rocks progressive transformation of primary minerals onto secondary ones takes place. It is generally connected with the migration of many chemical elements. Some of them are being released from the structures of primary minerals and they are included into the water solution and are removed from the environment of weathering rocks, others – on the other hand – are incorporated into newly formed minerals or are being sorbed on their surface. In this way, some of subordinate elements of parent rocks can be concentrated in final products of chemical weathering, whereas others are removed to a large extent. Lately, the practical aspect of this problem is often being discussed. More and more attention of users of industrial products manufactured from clayey raw materials focusses on the influence of these materials on human health and natural environment. In compliance with the users' expectation they should be safe and proecologic in character. This problem consists – among others – of the presence of such detrimental and even toxic elements as: actinides (uranium, thorium) and heavy metals in clayey rocks represented by kaolins and clays. This problem is the subject of this paper.

ACTINIDES

The natural radioactivity of clayey rocks is a result of occurring of natural radioactive isotopes in them. Among them an important significance play actinides, especially uranium and thorium.

Uranium occurs in clayey rocks in the form of mobile uranyl ion $[UO_2]^{2+}$ which often is sorbed onto different substances. In this process the most important significant are (in diminishing sequence): organic matter > hydrated iron oxides > phosphate minerals > clay minerals (Borovec 1974). Among secondary phosphates one should underline the role of minerals of crandallite group of which the presence in domestic kaolins was documented for the first time by Szpila and

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Dzierżanowski (1980). As far as other minerals are concerned, zircon $Zr[SiO_4]$ and copiapite $(Fe^{2+},Mg)Fe_4^{3+}[(OH)(SO_4)_3]_2\cdot 20H_2O$ play also an important role in the concentration of uranium (Wyszomirski 1992). Copiapite is easily soluble in water sulphate mineral. Characteristic yellow efflorescences of it appear sometimes in summer, rain-free periods on the kaolin surface, e.g. in the Lower Silesia in former *Andrzej* open pit in Żarów as well as in *Turów* brown coal pit.

Contrary to uranium, thorium occurs in clayey rocks in the form of weak mobile Th^{4+} ion. As it appears from studies on Lower Silesian kaolins, this element is usually noticed in zircon and in phosphate minerals of crandallite group (Wyszomirski, Janczyszyn 1992).

On the basis of studies on uranium and thorium in the Lower Silesian kaolins (Wyszomirski, Janczyszyn 1992) it appears that the content of these elements changes in the following limits: Th - 3,6-60 ppm; U - 1,9-13,9 ppm. These values – especially related to thorium – are greater as compared to the average content of these elements in clayey rocks. The latter amounts to 3-30 and 2-8 ppm, respectively (Wedepohl 1969). Kaolins from Wyszonowice near Strzelin in which kaolinite is mainly of post-biotite origin is characterized by the elevated content of thorium. It is well-known that biotite – and especially inclusions of zircon in it – are the carriers of this element. On the other hand, weak compact kaolinitic sandstone of *Maria III* deposit in North-Sudetic Trough owing to which domestic washed kaolin is obtained, can be characterized by low amount of uranium and thorium. This deposit is documented within white complex of sandy-clayey sediments, which in this area is distinguished apart from other complexes such as: grey, red and black ones (Górniak 1997). Kaolinite of the rock in question originated mainly as a result of chemical weathering of feldspars (Stoch 1988), which – as it is well-known – are distinctly poorer in actinides as compared to biotite. In consequence, even removing of quartz from this raw material during its industrial processing on washed kaolin does not lead to the distinct increase of actinides content. However, in some sandy-clayey rocks of North-Sudetic Trough the content of actinides is distinctly elevated. An example for it can be the distribution of this element in weak compact kaolinitic sandstone from one of boreholes, namely from G-9 (Fig.1). This distribution shows distinctly elevated uranium and

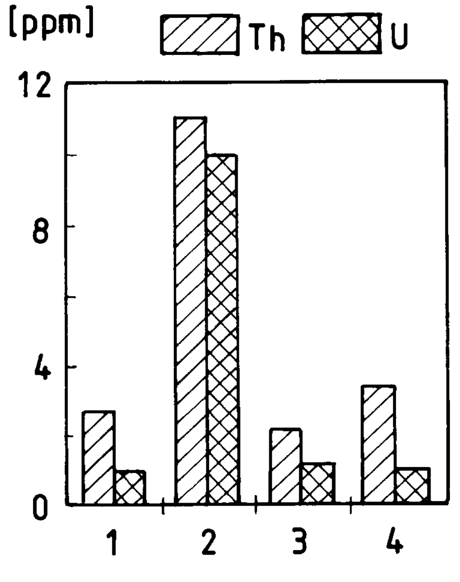

Fig.1. Uranium and thorium content in kaolinite sandstones of white (1), grey (2), red (3) and black (4) complexes from the North-Sudetic Trough (borehole G-9).

thorium content in rocks of grey complex. This fact should be related to the presence of phosphates of crandallite group which in subordinate amount occur in the rock (Wyszomirski et al. 1998-99). Moreover, studies of claystones of G-9 borehole representing various lithological varieties indicate the direct relation between crandallites and actinides content. Greater amount of actinides was also stated in claystone of the black complex which indicates the role of organic matter.

The content of U and Th determined by an example of some Tertiary and Triassic clays – mainly of illitic in character (Fig. 2) – is as follows: Th - 9.3-15.1 ppm; U - 1.8-5.2 ppm. Greater content of these elements, especially related to thorium, was noticed in Liassic clays of North border of Holy Cross Mts. (Wyszomirski et al. 1996) - Th: 17-28 ppm; U - 2.9-5.4 ppm. On the basis of comparison of actinides content in clayey rocks studied it can be seen that thorium occurs in distinctly greater amounts in kaolins. It can be related to the role of such minerals as zircon and phosphate minerals of crandallite group in the concentration of this element.

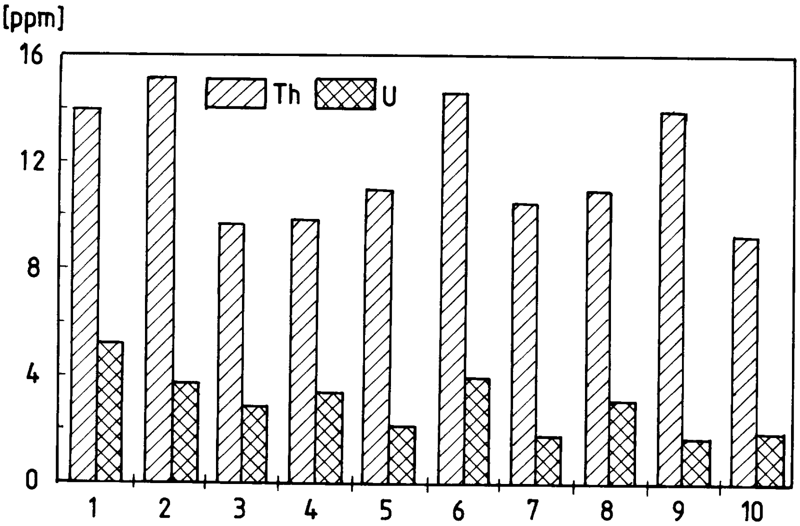

Fig.2. Uranium and thorium in some Polish Tertiary and Triassic clays. *Tertiary*: 1 – Gozdnica, 2- Jaroszów, 3 – Bonarka (Kraków), 4 – Zesławice, 5 – Wola Rzędzińska, *Triassic*: 6 – Baranów, 7 – Chełsty, 8 – Miasteczko Śląskie, 9 – Patoka, 10 – Rybna.

HEAVY METALS

In Lower Silesian kaolins from deposits: Turów, Wyszonowice and Bolesławice the content of heavy metals ranges in the following limits: Pb - <10-210 ppm, Cu – 1-42 ppm, Ni - <3-50 ppm (Szpila 1976). In these rocks the elevated amount of lead takes place. Similarly as Ba, Sr also REE and previously discussed actinides this element occurs in the structure of phosphate minerals of crandallite group (Szpila, Dzierżanowski 1980).

Clays studied being mainly represented by illitic ones, are differentiated according to the geological age. They are the rocks from the youngest ones namely Quaternary (Łężany deposit) up to the oldest i.e. Carboniferous shale (Kozłowa Góra deposit). Analyses carried out show that the content of heavy metals ranges in the following limits: : Pb – 15-200 ppm, Zn – 46-340 ppm, Cd – 1-19 ppm, Cu – 29-82 ppm, Ni – 10-76 ppm (Fig. 3). The highest concentration of lead, zinc and cadmium acompanying with the latter was stated in Triassic clays in the vicinity of Tarnowskie Góry in Upper Silesia. They are clays of Miasteczko Śląskie deposit and - particularly - of Rybna one. The latter clay lies directly on ore-bearing dolomites from which formerly Zn-Pb ores were exploited. In the clay of Rybna, the elevated content of other heavy metals, such as Ni and Cu, was noticed. In the mineral composition of clays in the vicinity of Tarnowskie Góry – apart from clay minerals (illite, chlorite) and quartz – calcite and ankeritic dolomite $Ca(Mg,Fe^{2+})(CO_3)_2$ were identified. The latter sometimes contains considerable admixtures of Pb, Zn and Cd that is typical of Upper Silesian Zn-Pb ore deposits. The elevated amount of heavy metals discussed in ankeritic dolomite from Triassic clays of Tarnowskie Góry vicinity is also in agreement with genetic circumstances. One of hypotheses corcerning the genesis of Upper Silesian-Cracow Zn-Pb ore deposits assumes that clayey rocks fulfilled the role of barriers causing the migration of water solutions rich in Zn and Pb within carbonate rocks (Sass-Gustkiewicz 1985). In this case, the precipitation of ankeritic dolomite is very probable in these parts of clay deposits which directly have a contact with ore body.

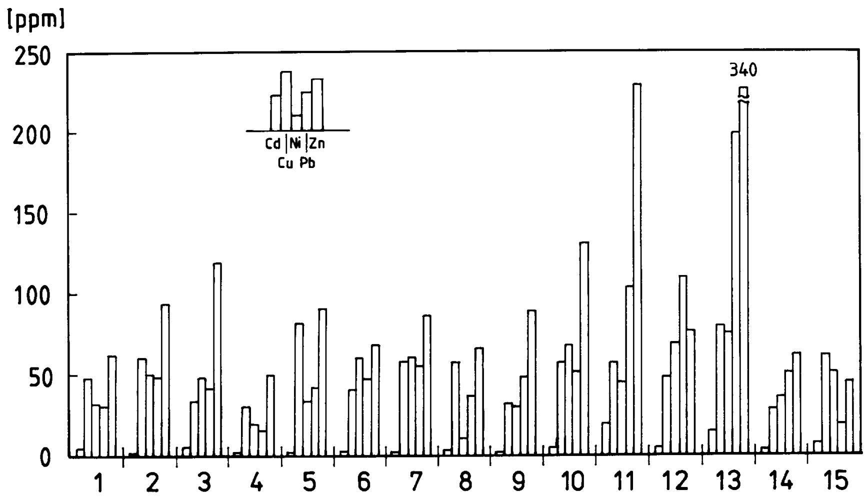

Fig. 3. Heavy metals in some Polish clays (sequence according to the draft). *Quaternary*: 1 - Łężany, *Tertiary*: 2 – Gozdnica, 3 – Jaroszów, 4 - Pawłów, 5 – Wola Rzędzińska, 6 – Zesławice, 7 – Turów II, 8 – Trepcza, *Cretaceous*: 9 - Wąwał, *Jurassic*: 10 – Grodzisko, *Triassic*: 11 – Miasteczko Śląskie, 12 – Patoka, 13 – Rybna, *Permian*: 14 - Sławków, *Carboniferous*: 15 – Kozłowa Góra.

Mechanism of concentration of heavy metals in clays from other deposits is undoubtedly different from the presented above. So, the cause of the elevated content of zinc in Dogger clay of Grodzisko deposit near Częstochowa can be mainly explained by isomorphic substitution $Fe^{2+} \Leftrightarrow Zn^{2+}$ in the structure of siderite which is subordinate mineral of this rock. On the other hand, the higher amount of zinc in clay from Jaroszów can be caused by sorption mechanism (Witek 1993). Finally, the carrier of heavy metals are also sulphide iron minerals (pyrite, marcasite) which often constitute the subordinate mineral component of many clays, especially illitic ones.

CONCLUSIONS

- Actinides – particularly thorium – occur in distinctly greater amounts in Lower Silesian (especially residual) kaolins as compared to clays. Probably it is caused by the role of such minerals as zircon and phosphate minerals of crandallite group in the concentration of this element.
- Elevated concentration of heavy metals (mainly Pb, Zn, Cd) – compared to other illitic clays – is typical of the Upper Silesian Triassic clays in the vicinity of Tarnowskie Góry which occur directly in the neighbourhood of Zn-Pb ore deposits.

Acknowledgements: The study was partially carried out within research project No. 11.11.160.989 of the University of Mining and Metallurgy Cracow financed by the Polish Committee for Scientific Research.

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