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Fluoride anion binding by natural lignite (South Moravian deposit of
Vienna basin)

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Abstract

Natural lignite from South Moravia was tested for the sorption of fluoride anion in concentration range from $5 \cdot 10^{-5}$ to $8 \cdot 10^{-4}$ mol/l. The lignite removes majority of fluorides and only about 13% of sorption is reversible upon leaching in pure water. Sorption data can be fitted by both Freundlich and Langmuir equations and both isotherms indicate presence of two principal sorption sites or steps. The sorption is fast, at least 90% of final sorbed amount is removed during the first ten minutes but kinetic data show a complex pattern with temporary increase of fluoride concentration. This is attributed to complexity of lignite-water interactions, lignite soaking and swelling in aqueous media. Foreign ions and pH showed only slight influence on the sorbed amount. Natural lignite can be considered as a potential low-cost defluoridation agent that is effective at various solution chemistries and also at low, but still over-limit, fluoride concentrations.

Keywords: Defluoridation; Fluoride; Lignite; Sorption

1. Introduction

Lignite belongs to the class of caustobiolites, substances of various coalification degree formed from original phytomass, and represents the youngest type of coal. In respect to its degree of coalification, lignite is found between peat and brown coal on the phytomass transformation scale. Lignite is typically used as a fuel. Similarly to any coal combustion, lignite burning represents a wasteful use of valuable raw material. Besides alternative use of lignite after some chemical or physico-chemical transformations, it can be used for non-energy purposes also in its natural state, which is the cost-effective way. Origin of lignite is the cause of its outstanding qualitative properties represented, e.g. by its high sorption ability and relatively high content of humic acids. Lignite thus could undoubtedly serve as a material for treating or preventing ecological accidents. In this work, binding of fluoride anion by the lignite mined in the Czech Republic is investigated

Fluoride anion, especially dissolved in water, belongs to elements of potential risk for the environment or human health. Although it has positive effect on the protection of teeth, too high concentration becomes harmful. The optimum fluoride level in drinking water set by The World Health Organization is between 0.5 and 1.5 mg/l, concentrations above the 1.5 mg/l (i.e., about $7.9 \cdot 10^{-5}$ mol/l) can lead to fluorosis (Díaz-Nava et al., 2003; Chubar et al., 2005). Fluorides can penetrate into the environment from phosphate fertilizer plants, glass etching units, aluminum smelters, and the fluorine industry. Various approaches especially to water defluoridation have been developed and published. The major techniques include precipitation, adsorption and ion exchange. Some of them are not so effective at low fluoride concentrations, which are still above the acceptable limit, e.g. the precipitation (due to the relatively high

solubility product), other may be cost-demanding. In Slovakia large areas of fluoride contaminated soils are found around an aluminum smelter plant, which contain about 30-35 mg/kg of fluoride, i.e. about six to seven times more than allowed by the local hygienic limit (Kobza et al., 2002). Those areas should be remediated preferably by some in situ technique using a suitable preparation capable of sufficiently tight fluoride binding.

Studies on low-cost and effective defluoridation agents are continuously reported (Sinha et al., 2003; Jamode et al., 2004a, b; Fan et al., 2003; Sarkar et al., 2006). Some of them investigated also coal, coal-related or carbonaceous materials. Sivasamy et al. (2001) studied a variety of coal-based sorbents including lignite. In the case of lignite they found a higher defluoridation in the pH range between 6 and 12. Fine coke and bituminous coal showed higher defluoridation efficiency at acidic pH values. At 90 mg/l of initial fluoride concentration, the removal efficiencies were between 77 and 85% with the highest one for the lignite. Capacities were between 6.9 and 7.44 mg/g (lignite 7.09), which is lower than that of the spent catalyst and fly ash, but higher than the activated carbons. All three investigated coal-based sorbents obeyed the Freundlich and Langmuir adsorption equations. Abe et al. (2004) studied fluoride sorption on activated carbons, charcoal, carbon black, and bone char. Percentages of removal for 200 mg of sorbent per 20 ml of the fluoride solution (20 mg/l) were between 0.4 and 17, while 82 for the bone char. Freundlich adsorption isotherm could be applied for data description. Adsorbed amount increased on increasing temperature or decreasing pH. Adsorption onto the bone char increased after adding NaCl. Cmarh et al. (2005) studied removal of fluoride using adsorbents produced from mining waste. The removal was favorable at low pH, adsorbent capacity was determined at 15.67 mg/g and the removal was between

20 and 80% (initial concentration 20 mg/l) depending on pH. Adsorption kinetics could be modeled by the Lagergren equation, adsorption obeyed Langmuir and Freundlich equations. Further details on other sorbents can be found below in Table 3 which compares published sorption performance of various sorbents with that determined in this work.

Our research is focused on development of non-energy applications of lignite that is mined in the South Moravia region of the Czech Republic. Among them, utilization of Moravian lignite as a sorbent is investigated and we have confirmed appreciable sorption capacity for both inorganic and organic sorptives (Pekař and Klučáková, 2003; Klučáková and Omelka, 2004). Special attention is devoted to lignite applications in its natural state with no additional treatment except perhaps crushing or milling and drying. Additional physical or chemical treatments involve additional costs and are not necessary if the effect of natural lignite is acceptable.

Here we report on affinity of the South Moravian lignite for fluoride anion. Although some information on fluoride sorption on lignites has been published our contribution is substantiated by several reasons. It is a part of our wider study on the sorption properties of the natural South Moravian lignite that, in addition, has not been tested for its interactions with the fluoride ions. This lignite is of a rather specific type. It is classified as an ortho-type characterized by a very low coalification degree and high contents of volatile combustible matter (Sýkorová and Michna, 2001; Honěk et al., 2001). Preliminary study demonstrated that the South Moravian lignite effectively binds fluoride anion in a broad concentration range (10^{-6} to 10^{-1} mol/l) with a very good sorption capacity (Pekař, 2006). Efficiency of lignite at low but still critical fluoride concentrations has not been investigated. Therefore, this study made a more detailed

analysis covering narrower concentration range just around the upper limit mentioned above, i.e. this is a study of natural lignite efficacy at low fluoride concentrations when usually sophisticated, cost-demanding methods should be used (Fan et al., 2003).

2. Materials and methods

Lignite from the Mikulčice locality (Czech Republic) was used throughout this study. Detailed characterization has been published elsewhere (Sýkorová and Michna, 2001; Honěk et al., 2001; Kučerík et al., 2003) only selected parameters relevant for sorption are reproduced here. Lignite was obtained as a crushed material which was dried, further milled and the fraction which passed the 0.2 mm sieve was collected for sorption studies and let to equilibrate with atmospheric moisture. The moisture content was then about 7%. Lignite particles had a broad size distribution with $d_{50} = 0.025$ mm and $d_{90} = 0.088$ mm. Its surface area is surprisingly low – about $3 \text{ m}^2/\text{g}$ (BET). Texture comprise mainly of macropores (95% of the total porosity determine by the mercury porosimetry).

Adsorption and desorption experiments were done in a batch arrangement at laboratory temperature ($25 \pm 1^\circ\text{C}$). Fluoride solutions were prepared from NaF (Fluka, p.a. quality) and deionised water at concentrations $5 \cdot 10^{-5} - 8 \cdot 10^{-4}$ mol/l. Lignite (0.5 g) was weighted into a plastic centrifuge test tube and 10 ml of fluoride solution were added. The suspension was shaken over a time period, centrifuged and concentration of fluorides in the liquid supernatant was determined. If desorption tests followed, then the solid residue in the test tube was washed with 5 ml of deionised water and then (after centrifugation and discarding the supernatant) 10 ml of fresh deionised water were added. The suspension was then shaken for 6, 24 or 72 h and, after centrifugation,

concentration of fluorides in the liquid phase was determined (no significant differences between results from different desorption times were observed).

Influence of foreign ions was tested using the same procedure but only with the fluoride solution at concentration of 10^{-4} mol/l to which NaHCO_3 , NaCl or Na_2SO_4 was added at final concentration of 10^{-2} mol/l. Calibration of fluoride electrode was in this case made with fluoride solutions containing the same concentration of respective salt.

Blank experiments made with lignite suspension in deionised water confirmed that lignite does not release fluoride in measurable concentrations.

Concentration of fluoride anion was determined using the combined fluoride electrode (Orion). TISAB buffer solution for fluoride determination was purchased from Theta'90 (Czech Republic). All other chemicals used to control pH or ionic strength were from Lachema (Czech Republic), p.a. quality.

Unless stated otherwise all experiments were done in duplicates. The largest relative difference between data measured in two replicates was less than 6%.

3. Results and discussion

Sorption isotherm is presented in Figure 1 and efficacy of removal for varying initial concentration is illustrated in Figure 2. Although fluoride sorption onto lignite is rapid (see also below) data obtained after 72 h of contact time are discussed here to ensure sorption equilibrium. Equilibrium fluoride concentrations were always below the limit of $7.9 \cdot 10^{-5}$ mol/l. The isotherm (Figure 1) is only slightly curved indicating that lignite sorption capacity is far from being exhausted which corresponds to our preliminary findings (Pekař, 2006) where maximum capacity was not achieved even at the initial fluoride concentration of 0.1 mol/l. The isotherm indicates two roughly linear parts

which can point to the existence of two types of binding sites or sorption mechanism. Relative fluoride uptake (Figure 2) decreases with increasing fluoride concentration but still remains above about 90%. Fluoride binding to the lignite is sufficiently tight, see Figure 3 which shows results of fluoride leaching. The amount released back to water increases with increasing initial fluoride concentration, i.e. with the sorbed amount, but most fluoride is not released. These results are promising for further future research on natural lignite application for the in situ remediation of fluoride contaminated soils.

Sorption data could not be simply and unequivocally interpreted using a single isotherm. This could be expected due to the heterogeneous nature of lignite and its complex, non-unique chemical composition. Plot of $\log a$ vs. $\log c$ (a is the sorbed amount and c is the equilibrium concentration) could be approximated by a straight line with the squared correlation coefficient (R^2) equal to 0.985. This would correspond, in the a - c coordinates, to the Freundlich isotherm. Yet better fit of logarithmic data could be obtained with two straight lines ($R^2 = 0.998$ and 0.993), i.e. two Freundlich isotherms, which probably indicate the presence of two main binding sites or mechanisms in accord with our previous results obtained on much broader concentration interval (Pekař, 2006). Data fitting in linearized coordinates of Langmuir isotherm, c/a vs. c , gave a straight line with $R^2 = 0.979$. The data also indicate two linear trends of different slopes but one of them is determined by two points only – the squared correlation coefficients are thus 0.999 and 1.000. Summarizing, the data could be fitted by both Freundlich and Langmuir isotherms, the former giving slightly better overall fit in the linearized coordinates, yet better fit is achieved with two Freundlich or Langmuir isotherms (see also Appendix). Parameters of all fits are given in Table 1. Although adsorbed amounts measured in this work stand with those few measured

previously at similarly low concentrations (see Appendix), estimated maximum adsorption capacities are fairly smaller than estimated and measured using a very wide concentration range (Pekař, 2006). This is an indicator that estimated isotherm parameters should be considered as empirical, formal values that should not be used outside the concentration range in which were determined.

Kinetic experiments showed that fluoride sorption is very rapid in principle (detailed study was made with the 10^{-4} mol/l solution). The first sample which could be analyzed was the sample taken 10 min after contacting the lignite and fluoride solution. During the first 10 minutes of sorption about 90% of the fluoride was removed from the solution. Subsequent evolution of the fluoride concentration showed some peculiarities and effects of complexity of lignite that definitely is not a homogeneous material of simply defined composition. Data from several kinetic runs are shown in Figure 4. Further decrease of the fluoride concentration, after the initial fast stage, is small and after 1-3 days the concentration can even slightly increase. Interaction of the natural lignite with fluoride solution and water is really complex. Definitely, besides the sorption also water soaking or absorption by the lignite occurs accompanied perhaps also by lignite swelling. Very fast initial decrease of the fluoride concentration indicates that diffusion processes play a minor role which corresponds to lignite macroporous structure. Visual observation clearly shows that the lignite is not a totally inert material upon sorption from aqueous solutions. It absorbs large volume of water or solution which was confirmed in independent experiments on suspending lignite in water and determining evolution of its moisture contents. Within 10 minutes the lignite regained water to the content about 40 % and after half an hour to 60-65 % (by weight), which is even more than in the fresh mined state (Sýkorová and Michna, 2001; Honěk et al.,

2001; Kučerík et al., 2003). On the other hand, during several first minutes of contacting with water the lignite demonstrated hydrophobic behavior – very poor wetting – and only then and under stirring or shaking the water soaking initiated. In our previous study on concentrated lignite dispersions (Pekař et al., 2005) surfactant was added to facilitate preparation of lignite pastes. Interaction of lignite with aqueous environment is thus not a simple process.

Complexity of lignite-water interactions and response of lignitic structure to moisture loss or gain is well known (Deevi and Suuberg, 1987). Norinaga et al. (1995) reported on affecting chemical and physical properties of lignite with dewatering or drying processes and found three different mobility types of water molecules in the lignite. It is well known that swelling behaviour of coal is different from that of a covalently crosslinked polymer and is caused by both covalent and noncovalent crosslinks or by some physical associations (Chen et al., 1998). Chen et al. (1998) demonstrated significant role of ionic forces and hydrogen bonding in the coal swelling. Successive dehydration and rehydration experiments (Pope, 1984) showed importance of change of lignite surface properties and relaxation of its structure in lignite-water interactions. Presence of cations can also influence swelling of lignite in water (Allardice et al., 2003). Norinaga et al. (1998) found three types of water in coals of different ranks and reported also on molecular modeling results confirming expansion-contraction conformational transitions of coal molecules in response to the change in the number of water molecules. Suuberg et al. (1993) published evidences that in addition water can affect diffusion processes within the lignite structure.

Although lignite soaks a large amount of water after 10 minutes of contacting, interactions of water with lignite structure (texture) evolve and water binding to lignite

structure changes. The fluoride ionic radius is 0.136 nm whereas main dimensions of water structures are between 0.29 and 0.36 nm (Gažo et al., 1977). It can be therefore speculated about that fluoride anions penetrate the lignite porous structure faster. Water molecules enter the structure more slowly, cause local swelling and osmotic effects. Initially, a more concentrated fluoride solution appears inside the lignite structure which is not far from its original state. The solution is then diluted with slowly penetrating water which is also able to enter structures enlarged by swelling and to displace previously penetrated fluoride ions. Changes in the lignite structure and texture caused by gradual penetration (slow diffusion) and action of water result in displacing some of the fluoride ions originally bound on the original structure or entrapped within it. Once the water-rich or swelled lignite structure is stabilized small part of fluoride can be re-sorbed within it.

We made also sorption experiments with pre-wetted lignite, i.e. lignite immersed in water before the sorption and containing about 60% of water. Temporal increase of the fluoride concentration after the fast initial decrease was also observed and was more distinct. This should mean that ion (electrostatic) and also osmotic effects play an important role. Lignite soaking and swelling in pure water and in electrolyte solutions are different. Moreover, the pre-wetting process removed from the lignite also soluble electrolytes as confirmed by the conductivity increase of the liquid phase. The pre-wetting experiments together with blanks confirmed that temporal concentration increase cannot be explained by dissolving fluorides that could be present in lignite. Sorption of fluorides onto lignite is not only a matter of their binding by some mechanism (ion exchange, covalent bond, hydrogen bond etc.) but is controlled also by other physical processes.

Kinetic data thus could not be fitted and interpreted with any established model. The initial phase of concentration decrease (the first 6 hours) could be described with some success using exponential functions, e.g. of Lagergren or second order type but their parameters are clearly formal and not able to explain the whole run and therefore are not given here. Instead we present an estimate of the initial slope of the fast concentration decrease determined from the initial concentration and the concentration measured after 30 minutes which was fairly reproducible and gives some idea on the rate in the most important part of the sorption process. The average slope from six replicates was -365 (14) $\mu\text{mol}\cdot\text{l}^{-1}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ (the value in parentheses shows average deviation from the mean).

Measurements described so far were carried out with no special pH control. The initial pH of fluoride solutions was about 6.5 and after equilibration it decreased to 5.2-5.4. Special experiments on the effect of pH were also made with pH equal to 2, 4, and 8 (pH was set by concentrated HCl or NaOH). Higher pH values were not used because the lignite starts to dissolve in more alkaline media (humic constituents are solubilized). The results showed that pH has a small influence on the fluoride uptake by the natural lignite, data indicate a slight increase in the sorbed amount with increasing initial pH (Figure 5) which agrees with findings of Sivasamy et al. (2001) for lignite and Das et al. (2005) for activated bauxite whereas most other sorbents show decreasing efficacy with increasing pH (see, e.g. Abe et al., 2004; Cmarh et al., 2005; Karthikeyan et al., 2005). More interesting is the change in pH after sorption equilibration, see Table 2. Regardless the initial pH its final value is about 5 which corresponds to “buffering” properties of natural lignite in both alkaline and acidic regions (Pekař et al., 2006). This may indicate that the change in pH (buffering) and the fluoride sorption are two independent processes and that the buffering ability of the lignite suppresses the effect

of pH on the fluoride sorption. Another hypothesis, substantiated by the double-line fitting of the sorption data, might be that two sorption active centers operate differently at different pH – each of them is preferred at different pH values. Whereas the increase in pH could be explained by an increase in concentration of hydroxyls which were exchanged with fluoride anions, the easiest explanation of the pH decrease would be by the effect of humic acids leached from the lignite in alkaline media. Consequently, the pH decrease really may not be related to the fluoride sorption process.

Addition of foreign ions at concentration of 0.01 mol/l had a little effect on the fluoride sorption (from the 10^{-4} mol/l solution). Uptake increased in about 2% upon NaCl addition, decreased in about 4% in NaHCO₃ and remained almost unchanged when Na₂SO₄ was added.

Our results show that natural lignite is an effective sorbent for fluoride anion working at various conditions of solution chemistry and capable to decrease also low fluoride concentrations that are, however, still above the recommended health limit. The fluoride binding is sufficiently tight and only a minor part is back-leached into water. The highest measured lignite sorption capacity was about 2.5 mmol/g (Pekař, 2006), which is several times higher than reported for other types of carbonaceous sorbents (Sivasamy et al., 2001). It is not easy to compare published sorption capacities due to their strong dependence on initial concentration and differences in experimental conditions. Table 3 collects just the best sorption effects of various fluoride sorbents reported for neutral pH (between 6 and 7) at laboratory temperature (between 20 and 30 °C) which were really measured or calculated from the Langmuir isotherm fit. As discussed above, the Langmuir capacity can be considered realistic only if surface saturation was really approached during equilibrium experiments. Lignite used in this

study belongs to the group of the most effective sorbents with the maximum sorption capacity at the order of tens milligrams per gram.

Whereas lignite sorption ability for metal ions can be easily understood and explained by abundance of carboxylic and hydroxyl group as confirmed also by quantum chemistry calculations (Klučáková et al., 2000), causes of the high lignite affinity to the fluoride anions are not fully clear. Sivasamy et al. (2001) suggested that fluoride can be bound to the coal surface by the ion exchange with the hydroxyl ions or through the hydrogen bonds to the hydrogen atoms of the surface functional groups. Ion exchange could be responsible for the increase of pH after the sorption observed in some of our experiments. Ion exchange can also explain the reversible part of the fluoride sorption. Decrease of pH during the sorption from alkaline and neutral solutions and irreversibility of bonding of major part of the sorbed fluoride indicate presence of also other mechanisms though the former can be explained by leaching of humic acids. The fluoride anion is known to form firm hydrogen bonds which could explain the irreversible part. Halogenide anions generally act also as donors of electron pairs and form various complexes. Consequently, various forms of ligand binding on the lignite surface can be suggested participating probably both in the irreversible and reversible parts of the sorption. The fluoride binding can be mediated also through metal bridges formed with oppositely charged metal ions present in the lignite.

To summarize, fluoride binding to lignite is not a simple processes and at least two main mechanisms operate. One should be the ion exchange, in agreement with Sivasamy et al. (2001), and should be the cause of increased pH during sorption. Ion exchange is reversible and explains the reversible part of fluoride sorption. The other mechanism could be some tight fluoride binding either by hydrogen bonding (Sivasamy

et al., 2001) or electron donating to lignite metallic constituents or organic functionalities of lignite humic structures. The uptake rate is determined primarily by the sorption reactions with (internal) diffusion playing only a minor role. Sorption process is accompanied by lignite swelling in aqueous media which affects lignite internal structure.

4. Conclusions

Lignite mined in the South Moravia region of the Czech Republic, in its natural state, has a remarkable affinity for the fluoride anion, under various solution chemistries. Binding of fluoride on the lignite is relatively tight and only minor part is leached into water. The sorption is effective also at relatively low fluoride concentrations which are still above health risk limit (1.5 mg/l) and the lignite enables to lower fluoride concentration below the limit. On the other hand, maximum sorption capacity is not achieved even at much higher concentrations. The lignite is therefore a potential cost-effective defluoridation agent that could be preliminary considered as a candidate also for in situ remediation of fluoride-contaminated soils where it can further serve as a soil amendment and conditioner due to its high contents of humic substances. Further research will be thus focused on lignite efficacy in fluoride binding and immobilization in fluoride-contaminated soil samples and on its selectivity in this environment containing other and potentially competitive sorptives.

Appendix

Two linear regions in measured data are shown in Figures A1 and A2 for linearized coordinates of Freundlich and Langmuir isotherm, resp.

Comparison of data obtained in our previous and this work is given in Figure A3. The two works overlapped in a very narrow concentration region therefore only two data points from the previous work could be shown.

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Figure legends

Fig. 1. Fluoride sorption isotherm on lignite

Fig. 2. Efficiency of fluoride removal from solutions of various initial concentrations (c_0)

Fig. 3. Results of fluoride leaching after its sorption on lignite from solutions of various initial concentrations (c_0)

Fig. 4. Decrease of fluoride concentration during sorption on lignite; averages of duplicates of four different runs. Initial concentration: 10^{-4} mol/l.

Fig. 5. Influence of initial solution pH on efficiency of fluoride removal from solutions of various initial concentrations (c_0)

Fig. A1. Sorption isotherm in coordinates of linearized Freundlich isotherm

Fig. A2. Sorption isotherm in coordinates of linearized Langmuir isotherm

Fig. A3. Data measured in this (triangles) and previous (Pekař, 2006; circles) work

Table 1

Parameters of Freundlich ($a = kc^n$) and Langmuir ($a = a_{\max}Bc/(1+Bc)$) isotherms determined fitting one or two isotherms

concentration range $\mu\text{mol/l}$	k $\text{mol}^{1-n}\text{l}^n/\text{g}$	n	B l/mol	a_{\max} $\mu\text{mol/g}$	R^2
single fit					
1 – 70	7.18×10^{-3}	0.64	4.70×10^4	17.9	0.985/0.979
double fit					
1 – 5.6	0.125	0.86	–	–	0.998
5.6 – 70	1.98×10^{-3}	0.51	–	–	0.993
1 – 46	–	–	6.08×10^4	15.0	0.999
46 – 70	–	–	9.14×10^3	37.6	1.000

Table 2

Initial and final solution pH. The final values are averages determined for initial fluoride concentration 10^{-3} and 10^{-4} mol/l; values in parentheses show the average deviation from the mean

pH	
initial	final
2.0	4.8(0.2)
4.0	5.1(0.2)
6.5	5.5(0.2)
8.0	4.8(0.5)

Table 3

Published sorption capacities for fluoride anion

material	temp. °C	highest sorption capacity		source
		measured	calculated	
Al-zeolite	30	10	37	Onyango et al. (2004)
La-zeolite	"	17	46	
acidified montmorillonite	30	40×10^{-2}	–	Agarwal et al. (2002)
thermally activated biomass	25	10	–	Sinha et al. (2003)
leaf powder biomass	29	50×10^{-3}	40	Jamode et al. (2004b)
lignite	30	2.4	7.1	Sivasamy et al. (2001)
fine coke	"	2.2	6.9	"
bituminous coal	"	2.6	7.4	"
bone char	25	3.0	–	Abe et al. (2004)
activated carbon from coal	"	30×10^{-2}	–	"
charcoal from <i>C. obtusa</i>	"	10×10^{-2}	–	"
coal mining waste	20	15	16	Cmarh et al. (2005)
double hydrous oxide ion exchanger	22	88	90	Chubar et al. (2005)
hydroxyapatite	ng	40×10^{-3}	4.5	Fan et al. (2003)
fluorspar	"	63×10^{-4}	1.8	"
quartz+Fe	"	60×10^{-4}	1.2	"
calcite	"	32×10^{-4}	39×10^{-2}	"
quartz	"	10×10^{-4}	19×10^{-2}	"
lignite	25	48	71	Pekař (2006)
lignite	25	29×10^{-2}	71×10^{-2}	this work

ng – not given