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THE IMMOBILIZATION OF SOLUBLE METAL SALTS

The Analysis and Microscopy of the Si-Al Condensed System with Nickel Waste

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ABSTRACT

This laboratory's investigation is focused on the disposal of the waste materials from different industrial sources. The presented work focused on the stabilization of Ni-solution in siloxo-sialate network explores the location of this toxic metal's ions in the solid samples obtained. The analyses of the Ni-ion's concentration and distribution are based on the detection through the voltmeter-stripping method. The results show the possibility of the inhibition and immobilization of a toxic waste material from the electro-plating plant even with a high content of nickel by using sol–gel reactions of kaolinitic aluminasilicates. A further detailed electron microscopy with a chemical elements' analysis (WDX) describes the possible structural configuration.

KEYWORDS: sol - gel, condensed system, wastes, siloxo-sialate network

INTRODUCTION

The microscopy of the material obtained through the polycondensation of siloxo-sialate network continues previous work (Hanzlíček et al., 2002) and is a part of extensive studies dedicated to the disposal of industrial wastes. The condensation of the network during the setting means that a chemical synthesis had taken place at laboratory temperature and pressure. This condensed system had the capacity to bind or encapsulate various solid materials (sand, mica, limestone and many other kinds of inert fillers) creating different types of solid matter (Babuškin, 1985; Sanz, 1998).

A further possibility is presented in this paper: The directly incorporated metal-ions are bound to the oxygen bridges into the structure network of alumina-silicates, using the principle of the sol–gel reactions in an alkaline medium. Aside from the quantitative leaching tests of samples, a study of possible bonding has been carried out by the microscopy of the sample's polished section. For this investigation of chemical elements and their distribution in the structured polymer chain, the WDX microscopy was used. Both methods could finally lead to the supposition of their role in the structural system. The WDX microscopy picture of the polished section's surface was compared to the distribution maps of selected chemical elements. The work should prove the estimated participation of the nickel in the siloxo-sialate network.

EXPERIMENTAL

The laboratory part

The materials observed were the product that had resulted from solidification through the sol-gel reactions of the activated clay, the kaolinitic waste raw material from the Kamenná Panna deposit, W-special-tm, provided by the company Keramost a.s. Most, which was dissolved in an alkali aqueous solution. These samples were in all cases prepared from the mixture of 100 g of clay and according to the following molar rate: 2.756 SiO_2/Al_2O_3, 0.7606 Al_2O_3/Na_2O and 15.746 H_2O/Na_2O.

To add nickel ions, the nickel from waste powder was dissolved in 40 ml of 1 M H_2SO_4. The concentration of the nickel input is shown in Table 1. (The solid waste material was obtained from the electro-plating plant of the producer's cooperative: DUP Pelhřimov.) The concentration of dissolved nickel was detected by the voltmeter stripping DPV method.

The water content required for the sample's preparation was in all experiments substituted by 40 ml of these acid Ni^{2+} solutions. The mixing part was performed in a kitchen food processor for 45 minutes. The resulting homogenous liquid matter was then poured into plastic containers, covered to avoid the rapid evaporation of water, and allowed to set. The solidification of the whole content took 16 hours at a laboratory temperature and pressure. After 24 hours the samples were taken out of the moulds and left to

Table 1 Results of Nickel Inhibition

Experiment Number			1.	2.	3.	4.
c_1	(g/l)	Input Concentration of Ni^{2+}	9.07	13.90	19.13	32.32
c_2	(g/l)	Extract Concentration of Ni^{2+}	$0.005 \cdot 10^{-3}$	$0.005 \cdot 10^{-3}$	$0.018 \cdot 10^{-3}$	$0.024 \cdot 10^{-3}$
m_1	(g)	Mass of Ni^{2+}in the Sample	0.36	0.55	0.77	1.29
m_2	(g)	Mass of Ni^{2+}in the Extract	$0.003 \cdot 10^{-3}$	$0.003 \cdot 10^{-3}$	$0.009 \cdot 10^{-3}$	$0.0012 \cdot 10^{-3}$
Ratio	(%)	$\frac{m_2}{m_1}100$	0.0008	0.0005	0.0012	0.0009
Efficiency Factor of Inhibition			35	56	21	26

dry for 5 days. The samples were then crushed and pulverized (to a grain size of less than 0.5 mm). The 50 g of each sample were leached in 500 ml of distilled water for 24 hours using a laboratory shaker. The content of nickel in the filtrated extract was then measured again by the voltmeter stripping DPV method.

Table 1 shows the results of Ni-ions concentration in the extracts and the conclusive inhibition of Ni-ions in siloxo-sialate networks. The factor of inhibition expresses the ratio between the concentration of metal ions incorporated into the network of aluminasilicates on one hand and the concentration of nickel in leached water on the other, proportionally calculated on the basis of the samples' weight.

The Microscopy

The polished area of the prepared sample with a content of Ni-ions was investigated in detail through a surface observation followed by a chemical analysis performed by the WDX and EDX microscopy. The WDX analyses were carried out under an electron microscope CAMECA, JEOL JXA-50A and with X-ray microanalyses EDAX DX Prime, under the following conditions of measurements: acc. voltage 20kV, probe current $1.4 \cdot 10^{-9}$ A. The comparison and analysis of EDX-photomicrographs was done using PC program Adobe Photoshop.

The Observation

To identify the distribution of a chemical element (each has its own WDX microscopy map), the maps were lapped over each other, which made it possible to compare the picture of the surface with a distribution map of a chosen element. The picture of the cut depicts the sedimentation of semi-dissolved clay particles surrounded by a homogenous condensed system. The presented network bonds that way into a firmly solid and hard material. The grain boundaries represent some bigger particles while the transformation of the amorphous phases through the sol-gel synthesis is represented by the smooth transiting shades of gray. See Figure 1.

Nickel Map (See Fig. 2)

The distribution map (Fig. 2) shows nickel located outside of the rest of the particles, which proves the distribution of Ni-ions mainly in the amorphous condensed system of a siloxo-sialate network.

Iron Map (See Fig. 3)

The iron map supports the idea of clay impurities, which are partially dissolved during the synthesis and partially left in non-homogeneities. Fe-ions are distributed in the siloxo-sialate network almost uniformly with the exception of some rare agglomerates. The substitution of aluminum by a part of Fe-ions, coordinated by tetrahedron, could also be considered in the condensed network that corresponds to the conception known from the natural aluminasilicates.

The 9 points of the EDX-analysis study (Fig. 4) yielded the concentration of Ni- and Fe-ions in addition to sodium, calcium and potassium, followed by sulfur and then aluminum and silicon. The analyses in the points No.1 - 9 of the sample surface identifying the elements are calculated as oxides. The average composition of inorganic polymer found among the particle sedimentation is in Table 3. Table 4 provides the presence of nickel and iron detected by EDX microanalysis of the nine points in Fig. 4.

DISCUSION

The presence of nickel could be detected only in the amorphous matter among the particle residua, see Fig. 2. The average composition of this inorganic polymer considerably differs from the classic kaolinitic clay composition and suggests that new solid matter created through the sol - gel reaction incorporates metals in its network, especially metal ions in a tetrahedral coordination.

This work does not discuss the maps of distribution of silicon and aluminum, because this presentation was focused on the possible metal encapsulation or incorporation into the siloxo-sialate

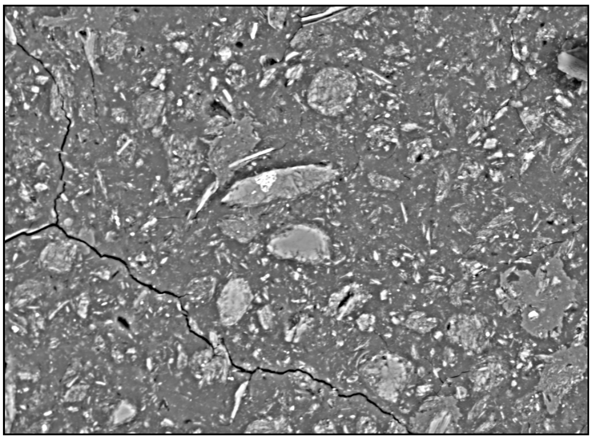


Fig. 1 Picture of the 1000 times amplified surface of the sample

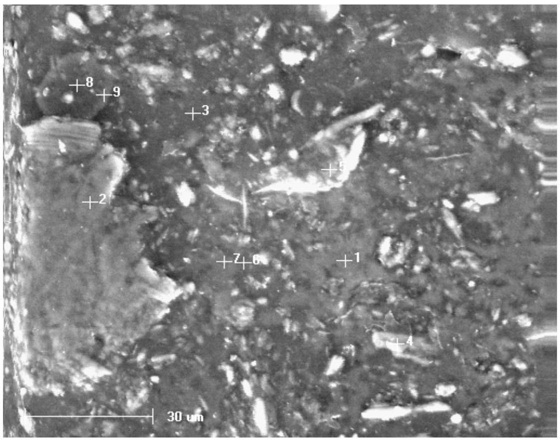
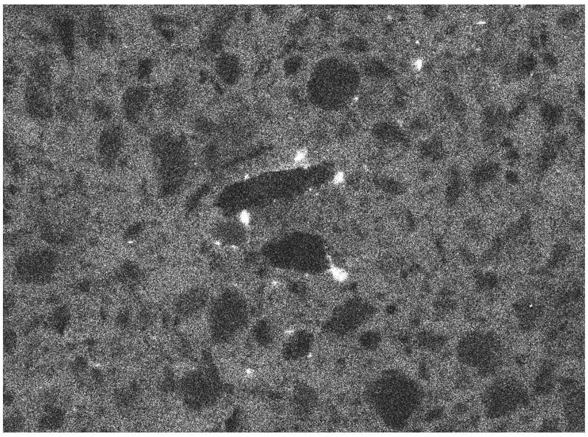
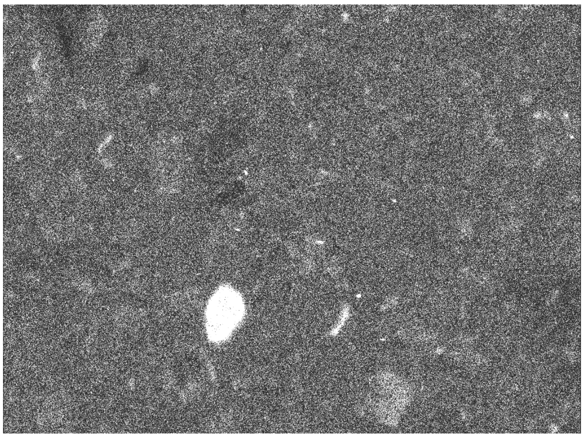


Fig. 4 Picture of the surface with point analyses by EDX microscopy



Ni

Fig. 2 Picture of the Nickel location



Fe

Fig. 3 Picture of the Iron location

Table 2 The Average Composition of Inorganic Polymer with Ni Content.

Oxide	SiO_2	Al_2O_3	Na_2O	Fe_2O_3	SO_3	NiO
Wt.%	60.78	26.75	5.63	1.72*)	1.87**)	1.33

*) The quantity of iron oxide is not the condition for the solidification of the sol - gel system**;** in the present case its content is caused by the presence of the impurities in the waste clay used.

) The detected quantity is a trace of sulfuric acid solution of the entering Ni (SO_4).**

Table 3 The Average Composition of Inorganic Polymer with Ni Content.

Oxide	SiO_2	Al_2O_3	Na_2O	Fe_2O_3	SO_3	NiO
Wt.%	60.8	26.8	5.6	1.7	1.9*)	1.3

*) The detected quantity is a trace of sulfuric acid solution of the entering Ni (SO_4).

Table 4 Detected presence of Ni^{2+} and Fe^{3+} (See Fig. 4)

Point No.	1	2	3	4	5	6	7	8	9
Wt.% NiO	1.8	0.6	2.2	0.5	0.8	1.3	1.1	1.3	0.8
Wt.% Fe_2O_3	1.4	1.9	1.9	2.1	1.9	1.8	1.9	1.6	1.3

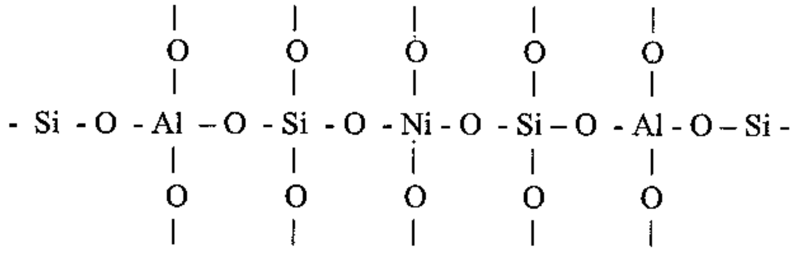
network. The presence of Al and Si ions is explicit and known from this laboratory's previous work (Hanzlíček et al., 2002).

It could be assumed that the transformation to the sol - gel system affects the main part of the smaller clay particles, which is accompanied by the disintegration of the bigger ones. The previous paper by Hanzlicek and Stienerova (2002) proves that it is the particles of less that 10 μm that are the most active, and their sediments are hardly identifiable formations of the condensed system.

From the presented results, it could be suggested that the higher the percentage of the dissolved clay particles, the higher the inhibition factor. The exceedingly small nickel content in the leached extracts and the evidence of its presence in the obtained solid matter lead to the conclusion that metal is chemically bound into the siloxo-sialat network. The possibility of precipitation of $Ni(OH)_2$ exists, but in the case where almost all $(OH)^-$ groups are consumed by the formation of the mono-, di-, tri- and polymers, such a possibility is lower than the one that suggests that nickel could enter in the way Cotton explained it. According to Cotton, in the case of aqueous solution of Ni (SO_4), nickel forms a $[Ni\ (H_2O)_6]^{+2}$ octahedral concourse of atoms. The energy level of the most stable configuration $t_{2g}{}^6e_g{}^2$ corresponds to the octahedrons, while the higher energetic level $t_{2g}{}^4e_g{}^4$ corresponds to the tetrahedrons. Their difference is explained (Cotton, 1964) as Δ_t (shift from t_g energetic level to e_g level), which is much lower than P energy (pair electrons' arrangement) on the e_g level. Although the high spin configuration $t_{2g}{}^4e_g{}^4$ depends on the differences between Δ_t and P energy, with $P < \Delta_t$, nickel in the form of a $(NiO_4)^{2-}$ tetrahedron could be stable and therefore enters the siloxo-sialate network.

This approximation is supported by Kocík et al. (1976), referring to tetrahedron structure of $(NiO_4)^{-2}$ observed in fused glasses. This form could be observed in the glasses with a high content of aluminum and alkalis (Volf, 1978). According to studies by Margaryan (1999), the tetrahedrons of nickel could be identified as the G – element (structurally glass). Our suggestion concerning the formation of the "Low-Temperature Inorganic Vitreous Melt" leads to a parallel with fused glasses. The observed bound mass and several other similarities (amorphous structure, silica base, process of condensation and shell-like fracture) support the parallel, but there are also big differences like porosity and first of all the temperature of origin among others. M.B.Volf presents: "To a certain degree, we can regard silica-fused glasses as polymers defined by a large number of SiO_2 molecules which are connected into a complex compound of polymer-like constitution in which the basic structural units of SiO_4 are spatially joined into one or more macromolecules." So, according to him, if the vitreous melt is defined as an amorphous polymer of a condensed system, then this unambiguously condensed system of polymers with an amorphous structure could be a specific form of vitreous melt, although its origin is not in the fusing and cooling processes.

The condensed system obtained through sol-gel reaction could offer the possible incorporation of nickel tetrahedrons as follows:



$$\begin{array}{ccccccccccccc} & & | & & | & & | & & | & & | & & \\ & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \\ & & | & & | & & | & & | & & | & & \\ -\mathrm{Si} & -\mathrm{O}- & \mathrm{Al} & -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}- & \mathrm{Ni} & -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}- & \mathrm{Al} & -\mathrm{O}- & \mathrm{Si}- \\ & & | & & | & & | & & | & & | & & \\ & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \\ & & | & & | & & | & & | & & | & & \end{array}$$

The suggested incorporation of nickel and the strength of a chemical bonded into the formatted network differ from the known acceptation of metals between the clay layers of certain three-layer silicates as montmorillonites.

CONCLUSION

The presented work was oriented to the analysis of the metal distribution in the condensed systems of siloxo-sialate network obtained through sol-gel solidification as a part of study dedicated to the disposal of waste substances. The most detailed study is focused on the explication of the bond strength and durability of the obtained matters that could immobilize toxic metals. The formation of the condensed systems and its ability of the incorporation of metals proved that the more dissolved clay particles, the higher the capacity of the immobilization. The location of the toxic metals in the siloxo-sialate network supports the previous opinion by the results presented. The toxic metals are not generally encapsulated in a condensed system or held by sorption between clay layers, but incorporated into the formatted amorphous network. This suggestion could explain high figures of the Factor of Inhibition and the extremely low concentration of nickel in leached waters.

The knowledge of the siloxo-sialate network ability to accept metallic and non-metallic elements could, in the final stage, be a part of the answer how to resolve the environmental contamination of the different industries, including acidic wastewater containing toxic metals.

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