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APPLICATION OF SODIUM WATER GLASSES FOR THE REMOVAL OF NICKEL SALTS FROM WATER ECOSYSTEMS*

WYKORZYSTANIE SZKIEŁ WODNYCH SODOWYCH DO USUWANIA SOLI NIKLU Z EKOSYSTEMÓW WODNYCH

Abstract: The properties of nickel, particularly toxic properties of nickel compounds were presented. Using the turbidimetric method, the systems containing sodium water glasses of different moduli and selected nickel salts were studied. It was demonstrated that high turbidity values in the studied systems indicate the reaction of Ni²⁺ ions with silicate forms and that is why sodium water glasses can be used to remove Ni²⁺ ions from water ecosystems, for instance wastewaters.

Keywords: sodium water glasses, turbidimetry, nickel salts, water ecosystems

Among the vast number of chemical compounds, not all of them are worthy of mass production, mostly because of their limited application possibilities, while their cost of production or synthesis is high. Sodium water glasses (sodium silicates) belong to the group of chemical compounds, which find versatile applications, though the knowledge of their properties and structure and particularly of their aqueous solutions is only slight [1, 2]. Also, there is lack of unequivocal opinions of researchers regarding the mechanisms of water glasses interactions [3, 4].

The analysis of recent literature indicates wide spectrum of studies, although because of significant topical scatter, obtained results do not lead to the solution of problems pervading for years [5].

Sodium silicates have to be counted among mass products of chemical industry, which in Poland did not yet find adequate application. Foreign production of water glasses, which are a foundation of many branches of economy is much higher than that

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in Poland. Sodium silicate belongs to the group of mass products, having in Poland the fundamental base for their production: silicon dioxide (SiO_2) in the form of sand and sodium carbonate (Na_2CO_3). Consequently, in Poland there are adequate conditions for the production of sodium silicates [2].

In Poland the sole producer of sodium water glasses is the "Rudniki" S.A. Chemical Plant, near Częstochowa. Five types of water glasses are produced there, denominated as 150, 149, 145, 140 and 137.

An attempt to use sodium water glasses for the purification of wastewaters their reactions with selected ions of transition elements

Literature concerned with the evaluation of interactions of water glasses solutions with selected electrolytes is very modest. There are publications on the influence of calcium and magnesium salts, ions terminating the hardness of water, on the behaviour of systems containing water glasses and iron(II and III) salts, because of the importance of silicates in the anti-corrosion protection of communal and industrial water grids [7–9]. In the previous studies in this area the following methods were applied: potentiometric with the use of ion-selective calcium electrode, viscosimetric, based on the viscosity measurements or the product of viscosity and density measurements for concentrated solutions, as well as turbidimetric method [3, 4].

The use of sodium silicates in the processes of water purification, particularly wastewaters, with variety of composition (including the content of inorganic salts) is sometimes hard to evaluate, it indicates the necessity to carry out studies on "water glasses – selected metal salts" systems.

It was mentioned that there are some results and attempts to evaluate the reactions of silicates with magnesium, calcium, iron(II and III) ions, however there is lack of studies regarding the reactions of water glasses with transition metal ions. Preliminary studies in this area indicate that the most useful method of studies is the turbidimetric method [6–8]. It is based on the formation of a soluble, colloidal silicate of a studied salt as a result of the reaction of soluble silicate forms with studied salts and the measurement of light intensity dispersed by the formed silicate. The ability to form the silicate of a studied salt and the nature of changes of the intensity of dispersed light depend on the chemical composition of the silicate solution and its silicate modulus (M_k).

Occurrence, properties, uses and toxicity of nickel

Nickel forms many individual minerals such as pentlandite $(\text{Fe, Ni})_9\text{S}_8$, chloanthite NiAs_2 , gersdorffite NiAsS [10]. Nickel is a silvery-white metal, in normal conditions does not react with air or water. It easily dissolves in diluted acids, producing Ni^{2+} ions and H_2 . Concentrated HNO_3 and *aqua regia* cause passivation of nickel [11]. In many different compounds exists on the +2 level of oxidation, such as NiO , $\text{Ni}(\text{OH})_2$, NiS , NiCl_2 , $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ [10,12]. Nickel is predominately

used as an additive for steel. Both pure nickel and its alloy with copper is used *eg* to make coins and everyday-use items, heating systems, rheostats and anti-corrosion layers. Nickel exhibits strong catalytic properties in the reactions of hydrogenation of organic compounds (the so-called Raney nickel) [10].

Nickel is not essential for the adequate functioning of most living organisms, however it was found that some plants cannot normally grow in the absence of it in soil. Mobility of nickel in the soil environment is strongly influenced by the granulometric and mineralogical composition of soils. Its occurrence in soil depends on the concentration of nickel in rocks. During the process of erosion, nickel is released forming mobile ionic form and is absorbed by iron and manganese hydroxides. Nickel is easily uptaken by plants, if it is present in soil in its mobile forms. In plants nickel is very mobile and is easily transferred to the upper parts of the plant. Vegetables accumulate more nickel than fruits. Excess of nickel causes the damage of assimilation apparatus – particularly in vegetables. The most frequent symptom of nickel excess is an illness caused by elimination of iron from physiological functions. Roots are also damaged, which become thicker, tawnier and do not grow normally. Moreover, this metal causes disruption of anion-cation equilibrium in green parts of the plants, which perturbs the metabolism of calcium and iron. Nickel uptaken by human organisms from food is in most part excreted, on the other hand nickel inhaled with atmospheric dust accumulates in lungs and causes damage to the mucous membranes. Lack of nickel causes the inhibition of growth and reduction of hemoglobin level in blood as well as epidermis changes and disruption of pigmentation [13]. Nickel is a microelement necessary for the proper functioning of an organism, is an activator of some enzymes and influences the hormonal activity. Nickel was thought to be a toxic, carcinogenic metal, however in 1970 it was demonstrated that is a microelement necessary for the proper functioning of an organism. In plant tissues nickel normally occurs in concentrations up to 3 ppm, while in animal tissues from 0.1 to 9 ppm. Nickel enters human organisms through alimentary and breathing systems [14]. Deficit of nickel causes degradation of liver, changes in pigmentation, deformation of bones, swelling of joints, reduction of oxygen absorption and increase of fatty tissues. Excess of nickel causes changes in the structure of nucleic acids leading to oral cavity, throat and lung cancer, as well as the so-called nickel eczema. It accumulates in lymphatic nodes, river phytoplankton and bottom residues and in tobacco leaves. One cigarette contains from 1.6 to 3.1 μg of nickel [15]. Concentration of nickel increases in the blood serum after an infarct and as a result of shocks and burns. Also in cancer tissue the concentration of nickel is elevated [14,15]. It was demonstrated that there is a correlation between the occurrence of oral cavity and intestine cancers and the concentration of nickel in potable water. That is why the emission of nickel to the environment as a result of combustion of fuels (particularly coal and oil), production of metallurgical and asbestos dusts, cigarette smoking, wastewater and sludge dumping from refineries, galvanizing plants and alkaline batteries production plants has to awake anxiety. This is the cause why there is a lot of nickel in soils and leafy plants.

Generally, nickel is not a component of natural waters. Its presence depends on the composition of soil. Nickel can occur in water in a dissolved form as a bivalent cation

or complex ions – mostly cyanide complex, and in an undissolved form as a cyanide, sulphide, carbonate or hydroxide. The concentration of nickel in surface waters is regulated by law.

For the determination of nickel, a colorimetric method with dimethylglyoxime is used in the range of nickel concentration from 0.2 to 20 mg/dm³ Ni. Samples have to be preserved by the addition of 2–5 cm³ of concentrated nitric acid to 1 dm³ of water. Cyanide containing samples may not be preserved. Nickel ions in slightly ammoniac solution, in the presence of strong oxidant (bromine) react with dimethylglyoxime, producing red-coloured complex compound. Intensity of coloration is proportional to the concentration of nickel. By the direct method nickel can be determined in concentrations from 0.2 to 5 mg/dm³ Ni [16].

Experimental

Sodium water glasses produced by Swedish company Eka-Chemicals in Bohus Div PK Sektor SC were used in this study [17].

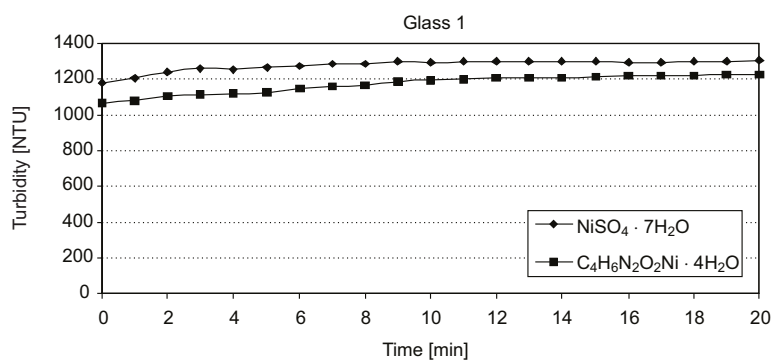


Fig. 1. Turbidity as function of time in the systems containing sodium water glass ($M_k = 3.243$) and studied salts

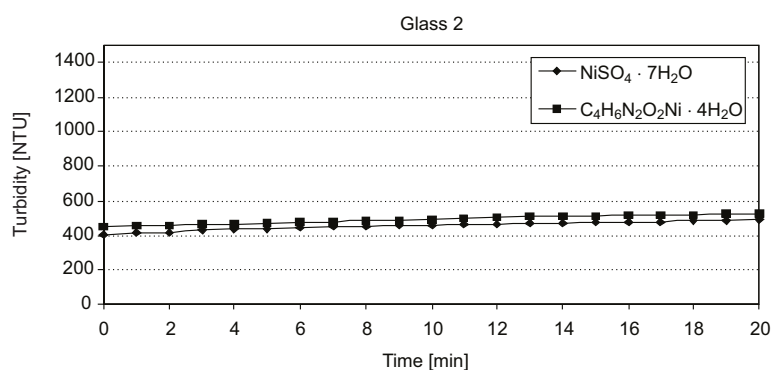


Fig. 2. Turbidity as function of time in the systems containing sodium water glass ($M_k = 3.264$) and studied salts

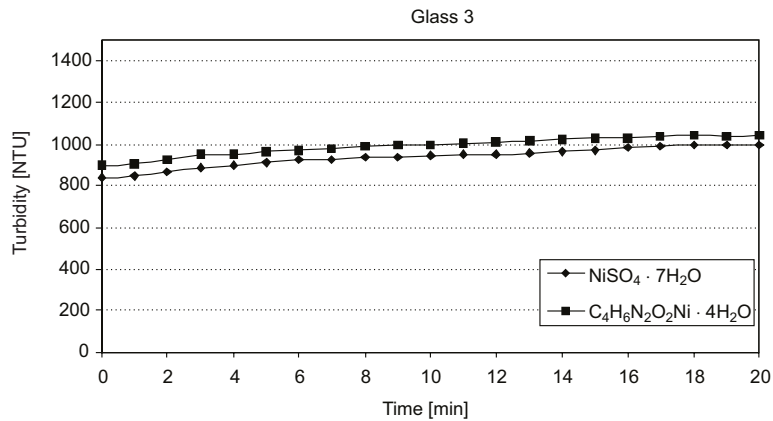


Fig. 3. Turbidity as function of time in the systems containing sodium water glass ($M_k = 3.289$) and studied salts

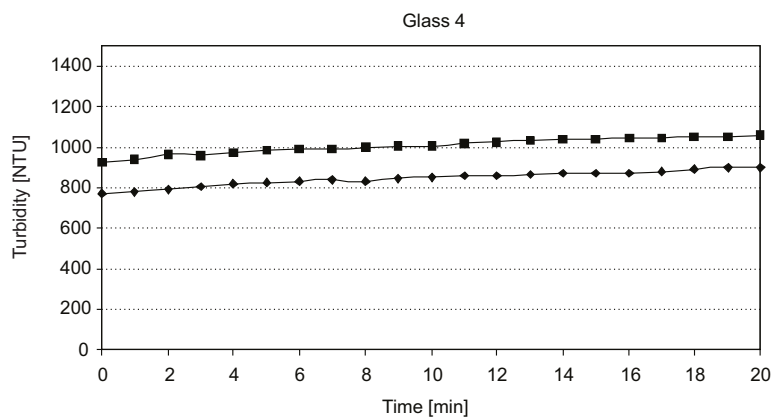


Fig. 4. Turbidity as function of time in the systems containing sodium water glass ($M_k = 3.412$) and studied salts

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{C}_4\text{H}_6\text{N}_2\text{O}_2\text{Ni} \cdot 4\text{H}_2\text{O}$ were used as nickel salts. The concentration of nickel ions was 8 mmol/dm^3 .

Experimental results in a form of turbidity curves are presented in Figures 1–4.

Conclusions

Addition of nickel salts to the water glass causes the precipitation of colloidal silicates, which are formed immediately, *ie* in the beginning phase of the measurement, without further significant increase of turbidity in time.

The type of silicate, *ie* its silicate modulus, molecular composition of its aqueous solutions and the type of used salt significantly influence the formation of colloidal silicates.

Taking into account the toxicity of nickel salts, sodium water glasses can be used to remove Ni^{2+} ions from aqueous media, such as wastewaters. High values of turbidity indicate significant reactivity of Ni^{2+} with silicate forms.

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WYKORZYSTANIE SZKIEŁ WODNYCH SODOWYCH DO USUWANIA SOLI NIKLU Z EKOSYSTEMÓW WODNYCH

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Abstrakt: Przedstawiono właściwości niklu ze szczególnym uwzględnieniem toksyczności jego związków. Metodą turbidymetryczną badano układy „różnomodułowe szkła wodne sodowe-wybrane sole niklu”. Wykazano, że duże wartości zmętnień w badanych układach wskazują na reagowanie Ni^{2+} z formami krzemianowymi i dlatego szkła wodne sodowe można wykorzystywać do usuwania jonów Ni^{2+} z ekosystemów wodnych, np. ścieków.

Słowa kluczowe: szkła wodne sodowe, badania turbidymetryczne, sole niklu, ekosystemy wodne