

Wiesław KOŹLAK¹

**EVALUATION OF POSSIBILITY
TO USE SODIUM WATER GLASSES
PRODUCED IN POLAND TO REMOVE Ag⁺ IONS
FROM AQUEOUS MEDIA***

**OCENA MOŻLIWOŚCI WYKORZYSTANIA
KRAJOWYCH SZKIEŁ WODNYCH SODOWYCH
DO USUWANIA JONÓW Ag⁺ Z MEDIÓW WODNYCH**

Abstract: Systems containing sodium water glass produced at Zakłady Chemiczne in Rudniki and silver nitrate were examined by turbidimetric method based on obtaining dissolved silver silicate. From turbidimetry waveform we obtained results indicating that silver silicate is formed immediately in initial phase of measurement and has no further increase of turbidity in time. The values of turbidity and surface tension of studied system depend on the value of M_k . Low-module silicates can be treated as more useful in removing Ag⁺ ions from water media.

Keywords: sodium water glasses, silver nitrate, toxicity, turbidimetry, tensiometry, colloidal silver silicates

In the Institute of Chemistry, Faculty of Civil Engineering, Mechanics and Petrochemistry, Warsaw University of Technology, the Plock Branch the systematic studies on the properties and structure of aqueous solutions of sodium silicate have been carried out for many years [1, 2].

Sodium water glasses possess innumerable application advantages [3, 4]. It was demonstrated that they can be used for the removal of toxic metals from the environment components, such as surface waters and soils. Because of their abundance and wide uses, the metals are grave pollutants of the ecosystems [5–9]. The harmfulness of metals is based on their ability to accumulate in living organisms and their chronic

¹ Faculty of Civil Engineering, Mechanics and Petrochemistry in Plock, Institute of Chemistry, Warsaw University of Technology, ul. Łukasiewicza 17, 09-400 Plock, Poland, phone/fax: +48 24 262 36 91, email: ich@pw.plock.pl

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toxicity. The health effects of regular intake of even trace amounts of heavy metals can manifest themselves after several months or even years. Children and ailing people are particularly susceptible to the toxic action of heavy metals [10].

In the Institute of Chemistry, studies were recently undertaken to evaluate the possibility to use sodium water glasses to remove toxic metals from, *ia*, aqueous media.

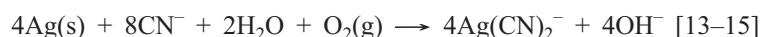
The aim of this study, being the continuation of widely scoped investigations, is the analysis of the possibility of reaction between different-moduli sodium silicates and Ag^+ ions.

Properties, toxicity and forms of silver ions occurring in waters

The Ag symbol is derived from the Latin name of silver, argentum. Silver (Ag) is a noble metal, rather neutral for living organisms. However, the excess of Ag damages cell membranes and causes the necrosis of liver tissues (similar to the effect caused by the lack of selenium (Se) and vitamin E), influences the concentration of Cu in kidneys and liver when the Wilson illness is ascertained (liver-lenticular degeneracy) and protects RNA from the excess of zinc (Zn). Moreover, the increase of silver amount in food causes the chromatosis of skin and mucous membranes (blue-greyish spots) called "agryria" and not harmful [11, 12].

Ag accumulates in coals (0.1–20 ppm), petroleum, zooplankton (10–20 ppm) and root tissues of some plants (up to 50 ppm). Cow milk contains typically 0.05 ppm of silver which can act as a bactericidal agent. Ag in the concentration of 25 mg/m^3 is toxic for microorganisms.

Silver is a rather rare element, occurring mainly as native silver, argentite (Ag_2S) and cerargyrite (AgCl). Only a small part of silver production comes from silver ores, it is mainly obtained as a co-product in copper or lead production. The main problem related to the production of silver from its ores is the transfer of non-active silver or its insoluble compounds into the solution. It can be achieved by blowing air through the suspension of silver ore in a diluted aqueous solution of sodium cyanide (NaCN). The reaction with native silver can be presented in the following way:



If cyanide ions were not present, oxygen would not oxidize silver to a higher oxidation state. In the presence of cyanide ions Ag^+ ion produces strongly bound complex ion, which is stable. In order to reclaim silver from the stable complex it is necessary to use strongly reducing agent, such as metallic aluminum or zinc in alkaline solution. Probably the following reaction takes place:



Solid silver appears to be nearly white metal because of its high glossiness. It is too soft to be used in pure form in jewelry or mintage, so it is used in alloys with copper.

By alloying silver with copper (10–20 %) an alloy of higher hardness is obtained, while the characteristic gloss of silver is conserved. Coins, jewelry and some other common use items are produced from this alloy.

Because of high price, some of the best properties of silver cannot be fully utilized, which are not exhibited to that extent by any other metal, such as very high thermal and electric conductivity. In the finely pulverized state silver appears to be black.

Silver compounds generally contain silver at +1 oxidation state. Ag^+ does not undergo significant hydrolysis in aqueous solutions, is a good oxidant and produces many complex ions, such as $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Ag}(\text{CN})_2]^-$, having linear structure. From the solutions of silver salts, under the action of bases, a brown oxide precipitates:



With the exception of AgF, silver halides are susceptible to light. That is why they are used to prepare photographic emulsions. The chemistry of photographic process is very complex. The basics of this process generally include: 1) exposure to light, 2) development and 3) fixing [13–15].

Silver as a metal resistant to oxidation is used to cover the surfaces of other, less noble metals. The production of silver coatings is an electrolytic process with the use of bath containing potassium silver dicyanide ($\text{K}[\text{Ag}(\text{CN})_2]$). Silver plating of glass, employed at the production of mirrors is a chemical process. It occurs by mild heating of plated material in ammoniac solution of silver tartrate [5].

Silver compounds occurring in waters in low concentrations exhibit bactericidal action. In high concentration silver is highly toxic. The possibilities of silver occurrence in waters are low (the concentration of silver in surface waters can not exceed $0.01 \text{ mg/dm}^3 \text{ Ag}$). The high price of silver causes that industrial plants using silver in their technological processes conduct the regeneration of silver from wastewaters and solid wastes. Silver can sometimes occur in mining waters and waste waters from factories producing photographic materials.

The determination of silver in water should be conducted as early as possible (less than 4 hours) after the collection of samples, because silver can become adsorbed on the walls of the container. If it is needed to store the samples they should be conserved by the addition of nitric acid.

For the determination of silver two methods are applied: rhodanine method and dithizone method [16].

Geochemical properties of silver are similar to those of copper but the frequency in geological structures is *ca* 1000 times lower than for copper. Silver is easily activated during erosion processes and subsequently precipitated in alkaline and sulphur rich environments. Despite its occurrence in mobile cations and anions, silver is bound in environments of $\text{pH} > 4$. Silver is partially accumulated biologically and its accumulation in some biolites is observed: 0.1–20 ppm in coals and 0.006–0.3 ppm in petroleum. Concentration of silver in ashes from some hard coals reaches the value even 200 times higher than in sedimentary rocks [11].

Silver in soils is easily sorbed by organic matter and on manganese concretions. Its average concentration in soils is between 0.03 and 0.1 ppm. In soils rich in organic substances the concentration of silver can reach even 2–5 ppm. Because of its low mobility silver is accumulated in surface layers of soils, particularly polluted ones. Highest levels of silver can be found in the areas near the mines of alkali metals. The

excess of silver is less harmful for plants growing on organic soils compared with those growing on organic ones.

The source of silver contamination can be galvanizing plants and other factories using the salts of this metal. Also communal wastewaters can introduce increased amounts of silver into soils [11].

There is few data relating to the occurrence of silver in atmospheric air. In the rural areas in England it was found in air in concentrations of 0.2–0.5 ng/m³ and the fall onto the ground of < 1 g/ha/year. Similar concentration of silver was (0.17 ng/m³) was found in air near coal fired power plants in the USA, which was related to the emission of ashes.

The attempts to use silver iodide to stimulate the condensation of water vapour in the atmosphere were the cause of periodic increase of silver concentration in air.

Concentration of silver in plants varies from 0.03 to 2 ppm because it is absorbed proportionally to its concentration in soils. Similarly to other heavy metals, silver is accumulated in roots, where its concentration may reach 50 ppm. Highest concentrations of silver are found in mushrooms.

Physiological function of silver is not yet researched but its excess damages cell membranes, inhibiting the absorption of other ions. Silver in the concentration of 5 ppm in bean leaves inhibited its yields while the symptoms of toxicity were not observed. Silver bonds easily with vegetable proteins, particularly with their sulfhydryl groups.

The presence of silver was found in all tissues of sea and land organisms, in concentrations ranging from 0.005 to 0.6 ppm.

Physiological function of silver in animal organisms is not known. The excess of silver causes the necrosis of liver tissues, symptomatically similar to the lack of selenium and vitamin E. It is the effect of antagonism between these two elements. Similar interaction takes place in relation to copper and probably to zinc [11].

Experimental

Sodium water glasses produced in Rudnickie Chemical Plant in Rudniki, Poland were used in this study. Their properties are presented in Table 1.

Table 1

Composition of sodium silicates

Type of water glass	Concentration [% wt.]		Silicate modulus M _k	Density (20 °C) [g/cm ³]	Substances insoluble in water [% wt.]	Chemical formula
	Na ₂ O	SiO ₂				
137	8.9	28.3	3.3	1.38	0.02	Na ₂ O · 3.3SiO ₂
149	11.8	33.1	2.9	1.51	0.02	Na ₂ O · 2.9SiO ₂
140	10.3	28.9	2.9	1.42	0.02	Na ₂ O · 2.9SiO ₂
145	12.4	28.8	2.4	1.47	0.02	Na ₂ O · 2.4SiO ₂
150	14.7	28.6	2.0	1.52	0.02	Na ₂ O · 2.0SiO ₂

AgNO₃ was used as silver salt. Concentration of Ag⁺ ions in studied systems was 8 mmol/dm³.

In this study turbidimetric and tensiometric methods were used.

Turbidimetry is a method used to measure the turbidity of a mixture by the measurement of absorption or dispersion of light on the dispersed particles [18, 19]. The method is based on the measurement of the changes of the intensity of light passed through optically inhomogeneous system.

The measurements were carried out for 20 minutes at the wavelength $\lambda = 610$ nm. The method and apparatus were presented in detail in earlier works [20–23].

Taking into account that the formation of optically inhomogeneous system and its stability depend also on the value of surface tension, this value was also measured. Surface tension is a work needed to unitarily increase the surface, related to intermolecular attraction forces, measured in a SI unit, N/m.

Measurements in this study were carried out with the use of Kruss K100 tensiometer, equipped with a platinum plate. In this method the liquid adhering to the plate is lifted until the moment preceding the breakage of contact between the liquid surface and the plate. At this time the weighing system records the highest value of force.

Results and discussion

Exemplary results of turbidimetric studies in the form of so called turbidity curves are presented in Fig. 1.

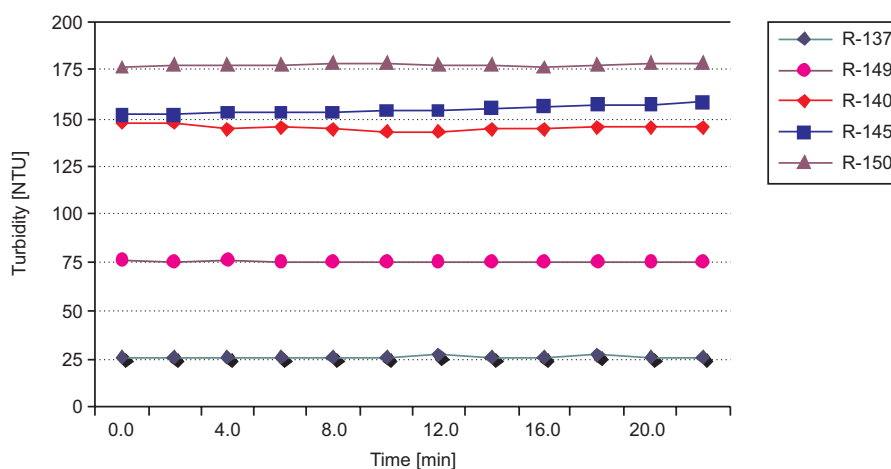


Fig. 1. The dependence between turbidity and time for the systems containing sodium water glasses and AgNO_3

From the course of turbidity curves it can be concluded that the silver silicate is formed immediately ($t = 0$) in the initial phase of measurement and no further increase of turbidity value in time is observed.

The results indicate that there is a correlation between *silicate modulus* M_k and *turbidity* (NTU). In the systems containing silicates of low moduli (150, 145) the

turbidity values fall into the range of 150–180 NTU, while silicates of high moduli (137, 149) give the turbidity from 25 to 75 NTU.

These observations allow the conclusion that silicates of low modulus ($M_k < 2.4$) are more useful in this application area.

The results of surface tension measurements are presented in Table 2.

Table 2

The results of surface tension measurements for “sodium water glass – AgNO_3 ” systems

Type of water glass	Surface tension [mN/m]	Standard deviation [mN/m]
R-137 ($M_k = 3.3$)	46.846	0.017
R-149 ($M_k = 2.9$)	47.528	0.021
R-140 ($M_k = 2.9$)	47.959	0.020
R-145 ($M_k = 2.4$)	49.201	0.010
R-150 ($M_k = 2.0$)	50.622	0.040

Basing on the data presented in Table 2 it can be concluded that there is a regularity of changes of surface tension as a function of silicate modulus. The values of surface tension decrease with the increase of M_k .

Obtained results indicate a significant influence of M_k on the behavior of “sodium water glass – AgNO_3 ” systems.

Conclusions

1. Addition of silver salts to sodium water glasses causes the formation of colloidal silver silicates. They are formed in the initial phase of the measurement and no further increase of turbidity in time is observed.

2. The values of turbidity and surface tension of “sodium water glass – AgNO_3 ” systems depend on M_k .

3. For the removal of Ag^+ ions from aqueous media, low-modulus silicates 145 and 150 are more useful.

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**OCENA MOŻLIWOŚCI WYKORZYSTANIA
KRAJOWYCH SZKIELEK WODNYCH SODOWYCH
DO USUWANIA JONÓW Ag^+ Z MEDIÓW WODNYCH**

Instytut Chemii, Wydziału Budownictwa, Mechaniki i Petrochemii w Płocku
Politechnika Warszawska

Abstrakt: Metodą turbidymetryczną polegającą na otrzymywaniu rozpuszczonego krzemianu srebra badano układy zawierające krajowe szkła wodne sodowe produkcji Zakładów Chemicznych w Rudnikach oraz azotan srebra. Z przebiegu krzywych zmętnienia wynika, że krzemiany srebra powstają natychmiast w początkowej fazie pomiaru i nie ma dalszego przyrostu zmętnienia w czasie. Wartość zmętnienia i napięcia powierzchniowego badanych układów zależą od wartości M_k . Krzemiany niskomodulowe można uznać jako bardziej przydatne w usuwaniu jonów Ag^+ z mediów wodnych.

Słowa kluczowe: szkła wodne sodowe, azotan srebra, toksyczność, turbidymetria, tensometria, koloidalne krzemiany srebra