

Assessment of possibility of using sodium liquid glass for removal of the most toxic metals: Pb, Hg, Cd from contaminated ecosystems

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Introduction

Metals are widespread in nature, where they occur in a form of ores, as energy state of their compounds is lower than their elemental form. For this reason, metals in an elemental form easily undergo corrosion, so they return to lower energy state. Only few metals such as: platinum (Pt), gold (Au), silver (Ag), mercury (Hg), copper (Cu) and sometimes iron Fe can occur in an elemental form. Their wide use causes that at the same time they are the source of ecosystem contamination, so the most important issue is the knowledge of their toxic properties [1] and the method of their disposal [2].

Metals in a form of pure elements are rather not toxic as they are practically not soluble in water. Only their vapors can easily penetrate human body through respiratory tract and skin that is why easily evaporating mercury is a poison.

Inorganic metal compounds that are easily soluble and strongly dissociating are the most toxic as they easily penetrate cellular membranes and placenta getting to organs, glands and fetus. They may cause proteins denaturation in dilute solutions (e.g. blood proteins, wounds proteins and mucous membrane) and in concentrated solutions they combine with protein and penetrate affected tissue eating them. While each metal has affinity to certain tissues, gland and organs [1, 3÷8].

Besides, the cations can bond with thiol groups –SH or carboxylic groups –COOH of enzymes or aminoacids causing changes in body metabolism.

Also the organometallic compounds, which among other cause allergy symptoms, are toxic.

Some of metals are carcinogenic - Cr, Ni, Co, As, Hg, Pb, Cd as well as radioisotopes [6].

Metals can cause acute intoxication, which can be noticed at once, and chronic poisoning. Metals such as Bi, As, Zn, Cd, Cu, Hg cause acute intoxication. Chronic intoxication can be caused by metals such as: As, Zn, Cd, Cr, Cu, Hg, Pb, Sn, Co, Ni, Mn, Se, Tl, Fe and Ag. Chronic intoxications that last for a long time in latent form are especially dangerous if they cause mutagenic changes or brain damages. This is for example lead Pb and mercury Hg intoxication. Chronic intoxications are very difficult to diagnose and very often hard to be cured [1, 4, 6].

Lead Pb, mercury Hg and cadmium Cd are the most toxic heavy metals. These are strongly carcinogenic elements which when occurring in environment in concentrations higher than permissible concentration, cause cancer. Besides, mercury and lead damage central nervous system, and cadmium causes hypertension – a disease that 20% of population in civilized countries suffer from. Pb, Cd causes a huge devastation in human population [1].

The objective of this paper is to present properties of the most toxic metals, their application and influence on environment. A trial of finding a method for reduction of Pb, Hg and Cd content in media and in environment has been undertaken.

Properties, application and impact of Pb, Hg and Cd on organisms and environment

Lead (Pb) is soft grey metal that dissolves in concentrated HNO₃, in H₂SO₄ at high temperature and in CH₃COOH in presence of oxy-

gen, and it is not soluble in water. It is resistant to corrosion, as in the humid air it covers with a thin layer of its hydroxide and carbonate.

Lead is a very toxic element. It is absorbed by organism through skin and respiratory tract. In organism it combines with thiol (SH) groups of proteins as well as it hinders bonding of iron into hemoglobin, stopping synthesis of proper enzymes. It damages central and peripheral nervous system the greater when the organism is younger. Besides, lead significantly shortens life and it is probably the reason for death due to a heart disease. Tests carried out on rats showed that lead shortens their life by $\frac{1}{3}$, i.e. by 30% [1].

Symptoms of lead intoxication are: excessive excitability, aggression, headaches, insomnia, lack of interest, deterioration of memory, physical and mental disturbances. People involved in production of lead and its alloys, goods made of lead such as batteries, pipes, bullets, paints as well as those, who live in a vicinity of motorways (up to 0.3 km) are especially exposed to Pb intoxication. Generally, there is a correlation between content of Pb in the air, soil and water and degree of industrialization in that area. Besides, this is the contamination of such a type that propagates to the entire ecosystem in the Earth. That is why lead-free petrol is manufactured [1, 10÷12].

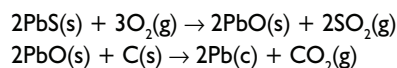
Lead, apart from Hg and Cd, is the most dangerous poison that gets into human environment. It is toxic to all live organisms. For instance collapse of Roman Empire is partly related to chronic lead intoxication due to use of lead pipes in aqueducts. As the watering system was used only by rich people it was a reason of decimation of aristocracy. Recently lead was identified as the substance contaminating environment due to its presence in car exhaust gases. Though total intoxication of a man takes place at relatively high doses of lead, danger of intoxication increases, as lead tends to accumulate in human body [3].

We have to notice that fuel tanks in aircrafts are corroding due to presence of microorganisms, as fuel for aircrafts does not contain lead tetraethyl. The conclusion is that Pb is also poisonous to microorganisms [1].

Besides, lead intoxication causes increase of Ca concentration in organism and decrease of Mg level. Thus deficiency of Mg in organism favors greater lead intoxication and the excess of calcium slightly controls Pb intoxication. By more intensive supply with Mg toxicity of Pb can be reduced and it facilitates elimination of Pb from organism. Besides, Mg²⁺ ions also reduce effects of hemolysis caused by Pb. Drinking water rich in CaCO₃ can protect organism to some extent. Studies have proved that drinking of such water reduces lead deposition in a skeletal system by up to 50% [6].

It is possible to treat lead intoxication and eliminate it from the organism by use of substance that dissolves Pb compounds, but this is a very dangerous treatment and about 2/3 children with brain damage treated with that method die [1].

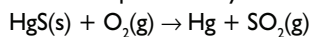
Lead occurs mainly as galena (PbS). Free metal can be obtained by roasting sulfide ore in air till its complete conversion into oxide, then oxide is reduced with carbon in a furnace similar to blast furnace, but a smaller one:



Raw lead can contain such contaminants like antimony, copper and silver. Generally, silver is recovered by extraction with melted zinc. If lead of high purity is required, it can be refined in an electro-winning process analogically to the process used in copper refining. Pure lead is a soft metal of low melting point and its fresh cross-cut has a silvery shine that quickly becomes matt after contact with air and takes blue-grey color. Matting is a result of creation of thin layer of oxides and carbonates. First of all, lead is used for lead batteries production, and as the component of alloys, to make typefaces and for soldering as well as to make lead white (hydrated alkaline lead carbonate). Lead white has excellent adhering and covering properties, so despite its toxicity it is still widely used [9 ÷ 14].

Mercury (Hg) is the only liquid metal in room temperature. The silvery liquid reacts with concentrated HNO_3 producing $\text{Hg}_2(\text{NO}_3)_2$ in low temperature and in boiling temperature it produces $\text{Hg}(\text{NO}_3)_2$ and nitrogen oxides. It also reacts with sulfuric acid (VI). It makes amalgams with metals, especially from I and II group. It is a very toxic metal for humans – it penetrates organism through a skin, respiratory tract and digestive system [1].

Cinnabar (HgS) is the only popular mercury mineral, from which free element is produced by roasting it in air:



Mercury is liquid in ambient temperature and its symbol expresses that fact as it comes from the Latin word *hydrargyrum*, what means 'liquid silver'. The liquid is not strongly volatile, but its vapor is extremely poisonous, so we have to avoid any longer contact with liquid mercury.

Liquid mercury has strong metallic shine, but it is not a typical metal as it has higher electric resistance in relation to other transition metals. However, in some cases, e.g. in production of electric contacts, its mobility is its big advantage that prevails over its low conductivity. Besides, due to its resistance to oxidation and its relatively high density as well as even dilatation with increase of temperature, mercury is used in thermometers and barometers [10 ÷ 12].

Liquid mercury dissolves many metals especially softer ones like copper, silver, gold and alkali elements. Formed alloys are called amalgams. Reduced activity of the metal dissolved in mercury is their characteristic feature. For example, activity of sodium in sodium amalgam is so low, that it can be stored in water and we observe only slight generation of hydrogen.

On cathode Na^+ reduces to Na^0 , which dissolves in mercury producing sodium amalgam. The produced amalgam is poured through a siphon to iron vessel containing water. Release of hydrogen on the iron surface is spontaneous, unlike in the case of mercury, so sodium amalgam reacts quickly with water producing NaOH as water solution and regenerated mercury. Basically, there is no mercury loss. However, in many cases waste mercury was washed out and was cumulated in rivers and lakes bottoms. If we don't undertake any measures to remove mercury, anaerobic bacteria present in a mud, will start to consume mercury producing dimethyl, mercury that is consumed in a food chain. Diatoms, having mercury compounds adsorbed on their surfaces are eaten by higher organisms and these are food for fish and fish is eaten by men and this is the end of food chain. Concentration of mercury increases at each stage of food chain [3 ÷ 6].

Other sources of contamination with mercury are the following: pulp and paper industry, laundries, seed treatment in agriculture, coal burning. In the paper industry phenylmercuric acetate $\text{C}_6\text{H}_5\text{HgOCOCH}_3$ is used in a production cycle. In the USA the method was abandoned due to the government decree that bans using of phenylmercuric acetate in production of paper which may have a contact with food. If safe use of paper cannot be guaranteed, then phenylmercuric acetate cannot be used. Laundries, especially those that clean linen goods sometimes use phenylmercuric acetate in mangling. Treatment of seed with mercury, despite the trade ban in the USA, is still

used, which was the reason of a tragedy. In some cases the seed, prepared for seeding by treating it with mercury, was colored in red to inform about danger in the case of consumption. Seed was then washed to remove the dye and used to feed animals and in the consequence to feed people with a meat poisoned with mercury from animals that were ill and were quickly sent to a slaughterhouse [4, 6, 8].

Coal contains about 1 ppm Hg. Burning of coal in the world is kept on the level of about $5 \cdot 10^9$ t/year, which means about 5000 T Hg emitted to atmosphere. That airborne pollutant explains why fish living in closed mountain lakes sometimes show surprisingly high content of Hg. Fish excretes mercury very slowly. Half-life of mercury in fish placed in fresh water is about 200 days, while in the case humans it is about 70 days.

Although the nature tried to hide mercury in a form of practically not soluble HgS , a man opened a tin of misfortunes by separation of the metal and also by burning fossil fuels. Not far ago there was a theory that elemental mercury is rather neutral and finally it transforms into not soluble sulfide that makes no harm. However, now we know that risk of contamination of environment by mercury is high.

Metallic mercury is not very toxic. However vapor of mercury is dangerous, especially after long exposition. Yellow sulfur that can be found spread in laboratories, where mercury is spilled, gives a chance to transform mercury into HgS and thus it protects against accumulation of even small amount of mercury vapor.

Inorganic mercury compounds, after dissolving are moderately toxic. For example, mercury chloride (II), when swallowed, causes injuries to digestive system and kidneys. Organic compounds, especially mercury dimethyl $(\text{CH}_3)_2\text{Hg}$, are especially toxic and their use as fungicides, as anti-mucus agents, for controlling mealworms and antibacterial sprays makes hazard to the environment.

Well known case of pollution of environment by mercury took place in Japan and it was identified as Minamata disease. Minamata is small fishing village on South-West coast of Kiusin. In 1953 a strange disease appeared there with symptoms of progressing pain in arms and face, night-blindness, dizziness, equilibrium disturbance and nervous breakdown, leading finally to death. Specialists linked these symptoms with consumptions of fish and after analyzing bottom sediments in the port they connected that fact with neighbor factory where HgCl_2 was used as the catalyst for production of polyvinyl chloride – commonly used plastic. It was concluded that mercury dimethyl $(\text{CH}_3)_2\text{Hg}$, produced in the result of bacteria action on waste slurries containing mercury, accumulated in fish tissues, was the reason of that disease [1].

What are the sources of majority of mercury pollution caused by people? It is difficult to answer the question as all depends on amount of mercury and on the method of handling with it as well as the method of its penetration to the environment. Chlorine industry in the USA is the biggest mercury consumer, it uses mercury cathodes in the process of electrochemical decomposition of sodium chloride in water solution [3].

Cadmium (Cd) is a soft metal of silvery white color and it is resistant to action of air (it covers with a protective layer of its oxide), it has lower electric conductivity than zinc. When warmed up to boiling temperature, it burns producing yellow-brown vapors of CdO . It easily reacts with acids. It is extremely toxic and carcinogenic, it deactivates enzymes bonding with thiol ($-\text{SH}$) groups and causing devastations in organism i.e. decalcification and deformation of bones, muscles atrophy (Itai-itai - *ouch-ouch* disease), loss of smell, impotence, blood hypertension and cancer, especially of the reproductive glands. It appears in urine just after injury to kidneys e.g. a week after intoxication i.e. from the moment of its introduction to organism. Together with kidneys injury, concentration of Cd in urine increases [1].

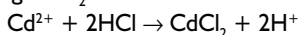
Symptoms of cadmium intoxication can appear after few years. They are as follows: xerostomia, sore throat, pain and pressure in chest, shortness of breath, cyanosis, circulatory and respiratory failure,

Chemical composition and formulas of studied water glasses

Type of water glass	Concentration, %wt Na ₂ O	Concentration, %wt SiO ₂	Silicate modulus, M _x	Formula of silicate Na ₂ O·M _x SiO ₂
1	9,2	29,1	3,264	Na ₂ O·3,264 SiO ₂
2	9,6	120	12,112	Na ₂ O·12,112 SiO ₂
3	9,1	29,0	3,289	Na ₂ O·3,289 SiO ₂
4	9,8	31,0	3,264	Na ₂ O·3,264 SiO ₂
5	7,0	22,0	3,243	Na ₂ O·3,243 SiO ₂
6	8,5	27,2	3,302	Na ₂ O·3,302 SiO ₂
7	8,5	28,1	3,412	Na ₂ O·3,412 SiO ₂

sometimes nausea, vomiting and headache. Cadmium intoxication is similar to intoxication with nitrogen oxides.

Cadmium penetrates organism through the respiratory tract and digestive system. Intoxication through the digestive system is often caused by eating food from a freezer having walls covered with cadmium. In stomach Cd reacts with hydrochloric acid of gastric juice giving CdCl₂:



Cadmium chloride causes acute inflammation of digestive system and necrosis of mucous membrane [1].

Cadmium has the properties similar to zinc, so both elements generally occur together. Flying ashes from purification of zinc through distillation are the main source of cadmium. Cadmium is more volatile than zinc and it evaporates before zinc and accumulates in first fractions of distillate. Covering of other metals e.g. steel, by its thin layer is the main industrial use of cadmium. It makes especially good protective coating in alkaline environment, as unlike zinc it is not amphoteric element and it does not dissolve in alkalis. Other important application of cadmium is production of fusible alloys like *Wood's metal* (melting point 70°C), used in fire sprinkle systems in buildings as fire-melted valve element [10–12].

Though cadmium is relatively rare element, it is numbered among the substances that significantly pollute environment. The most known case of cadmium pollution was in Japan called the *Itai-itai (ouch-ouch)* disease. The symptoms are: pain in bones and joints, waddle caused by deformation of bones – in later stages of disease bones are prone to complicated breaks. Contamination of water, food and air with cadmium causes pollution of natural human habitat. Cadmium accumulates in liver and kidneys and significantly deactivates enzymes that contain sulfur. Excretion with urine and through the digestive system is very slow, which means that cadmium is very dangerous. Recently cigarette smoke has been considered as the source of cadmium that is harmful both to smoker and to nonsmokers. High blood pressure as well as chronic diseases like bronchitis, emphysema, can be linked with a long-lasting intoxication with small doses of cadmium [3, 15–17].

Information about action of sodium silicates with inorganic electrolytes

In the literature there are not many studies devoted to the conditions of generation and properties of silicates of metal cations. First mentions can be found in the work of *Funka and Thilo* [18] and they concern production of flocky, amorphous precipitate Ca(H₃SiO₄)₂ produced in the result of reaction of 0.1 mol/dm³ NaH₃SiO₄ solution with calcium chloride solution.

On the basis of result of studies on production of silver silicates it was shown [19] that in diluted solutions of silicates the precipitates are produced, in which the silicate is the monomer (H₃SiO₄¹⁻). At higher concentrations of silicates, silicate polyanions appear. Increase of polyanions concentration, in the result of condensation reaction, initiated by addition of salt [20, 21], leads to precipitation of sediments (silver or calcium silicates). However, in those sediments we cannot find any polyanions and that makes determination of character of “silicate - Ca²⁺, Ag¹⁺” bond impossible.

In the result of further studies, especially with use of spectroscopic

methods, among others, ²⁹Si NMR spectroscopy, it was found that in determination of reaction of silicates with metal cations, molar weight of cations should be taken into consideration. It was found that possibility of creation of pair “silicate – M¹⁺” reduces together with increase of molar weight of M¹⁺ ion. Silicate condensation, caused by weakening of electrostatic repulsion between anions, in turn, favors the grouping in pairs of alkali metal cations, which hinder formation of silicates in the order sequence from Na to Cs [22, 23].

Also the different impact of cations and anions on changes of depolymerization rate of silicate polyanions, was revealed. So, reduction of the rate of the process takes place at increased cation activity in the following order:

Na¹⁺, K¹⁺, Mn²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Zn²⁺, Ni²⁺, Ce³⁺, Cu²⁺. Chlorides of mentioned metals were used as salts [24].

On the basis of analysis of interaction of different silicate forms and selected tetravalent and trivalent ions e.g. Al³⁺, B³⁺, Zr⁴⁺, Ti⁴⁺, it was suggested to use silicate water solution in anticorrosive protection [25].

Present studies on interactions of liquid glasses and selected inorganic electrolytes enabled concluding that introduction of metal ions or different electrolytes to liquid glasses solution causes series of reactions that change properties and sometimes the structure of silicate solutions [21, 26–29].

In the last projects of the author, attention was paid to the systems “sodium liquid glass – selected salts” of among others elements of II group and iron (II, III) [19–21]. There are no at all any studies on transition elements.

The first trials of studies on that [34, 35] indicate the necessity of continuation of such studies, as in spite of insufficient knowledge about formation of silicates of different metals, it is most probable that further research work on interactions between liquid glasses and salts of selected metals will give a chance to use them in new branches of industry e.g. in treatment of industrial and municipal wastes.

Experimental part

Sodium liquid glasses, manufactured by Swedish factory Eka-Chemicals in Bohus Div PK Sektor CS, of the chemical composition given in Table 1, were used.

Manufactured concentrated solutions were used in tests. The following nitrates were selected: Pb(NO₃)₂, Hg(NO₃)₂ and Cd(NO₃)₂, as they have good solubility. They are listed in Table 2.

Table 2

Salts selected for the study

Salt	M, g/mol	Amount of salt, g	Concentration, mmol/dm ³ salt (cation)
Pb(NO ₃) ₂	331,20	2,65	16
Hg(NO ₃) ₂ ·H ₂ O	342,32	5,48	16
Cd(NO ₃) ₂ ·H ₂ O	308,49	4,94	16

The following systems were used:

- sodium liquid glass - Pb(NO₃)₂

- sodium liquid glass - $\text{Hg}(\text{NO}_3)_2$
- sodium liquid glass - $\text{Cd}(\text{NO}_3)_2$

Turbidimetric method [9, 30 ÷ 35] seems to be the best method for testing physicochemical properties and the structure of liquid glasses and their water solutions as well as the systems containing silicates of alkali metals [13 ÷ 17, 30 ÷ 37] and that method was selected for testing from many other methods that are used. The method consists in obtaining soluble, colloidal silicate of tested substance produced in the reaction of soluble silicate form with the tested salt and in measuring intensity of scattered light passing through obtained silicate of tested salt. Ability of silicate formation of tested salt and the character of changes in intensity of scattered light depend on composition of silicate solution and M_k . Presence of impurities i.e. foreign ions added in the technological process of liquid glass production has a great impact on the reaction. The method is based on measurement of turbidity of tested system in a function of time. Turbidity of e.g. liquid glass is directly associated with light scattering theory. This optical property defined as turbidity is an interaction between light intensity and particles suspended in a solution.

Description of measurements

To 100 cm³ of distilled water 0.3 cm³ liquid glass was added and the mixture was stirred for 2 min (magnetic stirrer). 33.3 cm³ of solution of tested salt of concentration equal to 16 mmol/dm³ was added to such obtained mixture after 15 min - stirring vigorously for 0.5 min. After quick filling of a dish (that was previously thoroughly wiped to remove any stains and finger prints) the measurements of light scattering for wave length 455 nm, were carried out for 30 min. For each type of silicate the final result was an average value from three measurements.

Test results and discussion

Measurements of turbidity for tested systems were presented in Figure 1 ÷ 4.

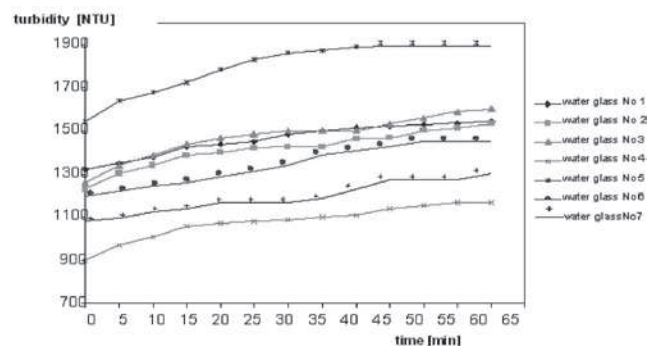


Fig. 1. Impact of lead nitrate on turbidity of liquid glasses

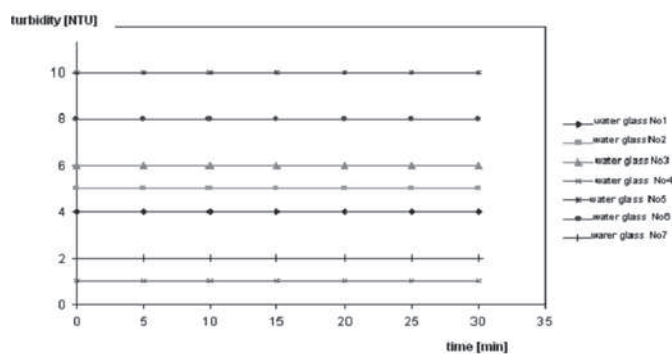


Fig. 2. Impact of salts of mercury on turbidity of liquid glasses

Different values of turbidity were obtained in all tested systems: the highest was for liquid glass No. 5 and the lowest values were obtained for liquid glasses – No. 4 and 7.

Character of turbidity curves is similar and we can observe increase of turbidity in time.

We have to admit that in the case of formation of colloidal lead silicate, about 2-9 times and 700 times higher turbidity, comparing to cadmium and mercury respectively, was observed.

Irrespectively to the type of tested silicate, presence of mercury (II) salt has a slight impact on turbidity and in all tested systems with mercury nitrate (II) turbidity values are 5-10 NTU (Fig. 2) (practically within the error limits).

The similar results were obtained in earlier work, when testing the systems “sodium liquid glass – magnesium salts” [36] and “sodium liquid glass – manganese salts” (II)” [33]. Thus we can conclude that colloidal mercury silicates, similarly to silicates of magnesium and manganese do not form.

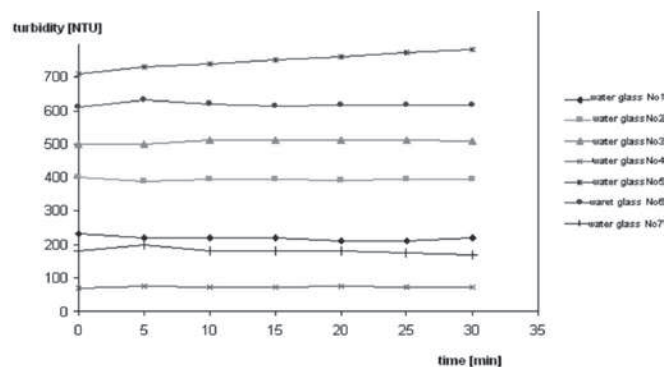


Fig. 3. Impact of cadmium nitrate on turbidity of liquid glasses

Similarly to the case of $\text{Pb}(\text{NO}_3)_2$ turbidity depends of type of liquid glass. Different values of turbidity was obtained: the highest was for liquid glass No. 5 (above 700 NTU) and liquid glass No. 6 (about 600 NTU), and the lowest value for liquid glass No. 4 (< 100 NTU). Character of turbidity curves is similar and we do not observe significant increase of turbidity in time. Cadmium silicates are formed at once i.e. at the beginning of measurements.

Conclusions

Results of studies enable drawing the following conclusions:

1. Addition of lead salts and cadmium to liquid glass causes precipitation of colloidal silicates that are formed at once i.e. at the beginning of measurements without further increase of turbidity in time in the case of cadmium.
2. Addition of mercury (II) salts to liquid glass leads to precipitation of colloidal silicates. The similar results were obtained earlier [31, 33] as in the case of magnesium and manganese salts.
3. Type of silicate and molecular composition of its water solutions have a significant impact on formation of colloidal lead and cadmium silicates.
4. Considering toxicity of metals Pb, Hg and Cd as well as their salts, the liquid glasses can be used to remove lead and cadmium ions from media like industrial and municipal waste sewage.

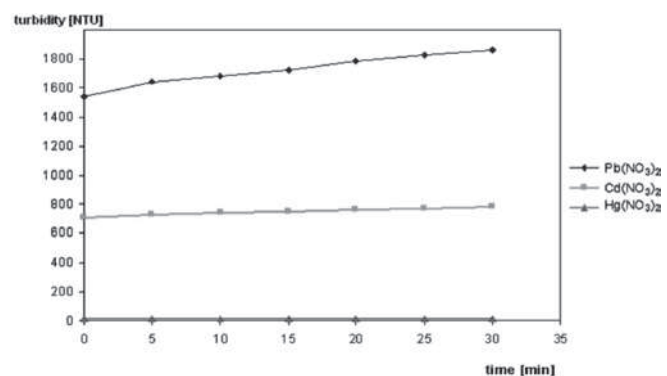


Fig. 4. Comparison of exemplary values of turbidity in “sodium water glass No. 5 –selected salts” systems

Summary

In studies on interaction of different modules liquid glasses with salts of selected metals, among others from II group, iron and manganese, it was found that in most of cases colloidal silicates of those metals are formed.

Presented results in the work should initiate further studies, especially extending them by salts of transition elements. They can create possibility of broader use of liquid glasses, among others, is solving environment protection problems especially, when it was found that [37] that liquid glasses are environmentally friendly.

Broad use of metals and their salts causes pollution to ecosystem, so there should be effective methods for removal of those unwanted metals from media.

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