Presence and impact of silica and organics in uranium in-situ leaching solutions

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Abstract. All uranium deposits of Uzbekistan mined by in-situ leaching (ISL) method belong to the so-called sandstone type and are formed on the redox barrier, with the Loyliken deposit, belonging to the so-called basal type, formed on the gley barrier, and all the rest, belonging to the roll type - on the complex gley-sulfur-hydrogen barrier. In all cases, the initial reducing agent is carbonized plant detritus (CPD), which is charred plant flakes scattered in sandstone, usually not exceeding 1 mm in cross-section - with the difference that at the gley barrier it is the direct uranium reducing agent, and at the gley-sulfur barrier a significant part of uranium is reduced by hydrogen sulfide, which is a product of biochemical reduction of sulfate ions contained in formation water by the same CPD (the so-called sulfate-reduction reaction). Among other conditions necessary for the formation of conditioned uranium mineralization, it is required that the CPD content in the formation is not less than 0.05% per organic carbon (Corg). At the same time, uranium concentration in almost all sandstone deposits of Uzbekistan is comparable to Corg concentration.

1 Introduction

In exogenous processes of ore formation an important role is played by geochemical barriers - those areas of the Earth's crust, where at a short distance there is a sharp decrease in the intensity of migration of chemical elements and, as a consequence, their concentration. Such a definition of a barrier is given by A.I. Perelman, the founder of the doctrine of geochemical barriers.

Almost all exogenous ore deposits are formed on one or another geochemical barrier. In particular, uranium mineralisation can be formed on evaporative (evaporation), neutralisation, sorption and, most often, reduction barrier (or redox barrier), which is usually divided into two subspecies - gley and hydrogen sulphide.

At the same time, uranium concentration in almost all sandstone deposits of Uzbekistan is comparable to Corg concentration.

At a purely gley barrier uranium is deposited almost exclusively in the form of uranoorganics, and uranium minerals are formed mainly in the form of pseudo morphoses after complete decomposition of its organic component, whereas under the action of

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hydrogen sulphide there is direct deposition of uranium from groundwater in the form of coffinite U(SiO4)1-X(OH)4X and pitchblende UO2+X. Nevertheless, even at the roll deposits on average about one third (from 19% at Beshkok to 48% at Loileken) of uranium is present not in mineral but in the uranium-organic form.

2 Methods and materials

The process of plant detritus carbonisation follows the same regularities as for other plant materials, so that in sandstones located at depths of up to 1000 m, the chemical composition of CPD is lignite (subbituminous) coal, which is the end product of plant residue decomposition at shallow depths - it is metamorphosed into hard coal only at high temperature and/or pressure, i.e. at great depths or in the volcanic zone (in the latter case anthracite and even graphite formation is possible).

Wood consists of cellulose fibres impregnated with lignin, which is a mixture of aromatic polymers of related structure (Figure 1). In nature, during the decomposition of plant residues, cellulose is first of all annihilated (from Latin annihilatio - destroyed) - its complete disintegration without the formation of solid residue. Lignin decomposes much slower, and in stages, with the formation of a number of intermediate products - so-called humic substances (HS), which are a very complex mixture of macromolecules of variable composition (with preservation of the aromatic base of lignin) and irregular structure (Figure 2 and 3).

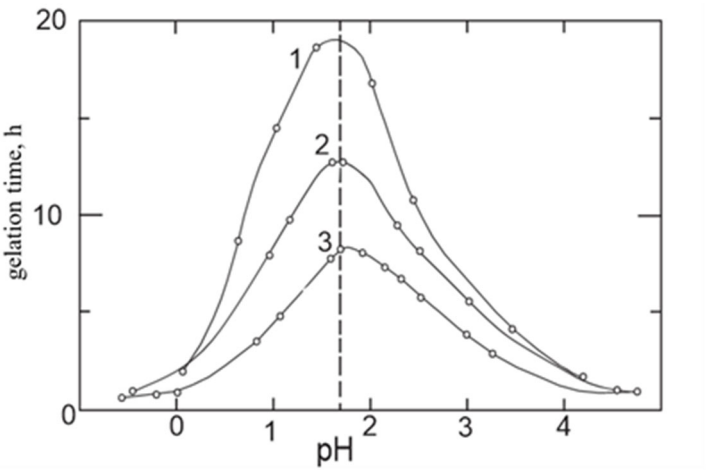


Fig. 1. Dependence of gelation time on pH for silica sols prepared from sulphuric acid and sodium silicate at different silica sol concentrations: 1 – 1,08 M (65.4 g/L); 2 – 1.33 M (79.8 g/L); 3 – 1.78 M (106.8 g/L).

In productive solutions (PS) of uranium ISL, silicon can be present simultaneously in various forms and states, therefore, in accordance with the recommendations of the most representative work on this subject - monograph by U.Z. Sharafutdinov - for convenience and simplicity, the term “silica” will be used to denote silicon dioxide SiO_2 in all its forms (crystalline and amorphous, anhydrous, hydrated and hydroxidised).

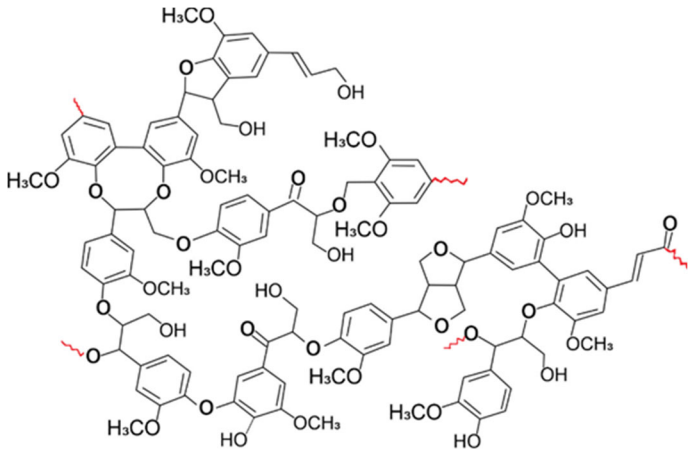


Fig. 2. A hypothetical structure of lignin.

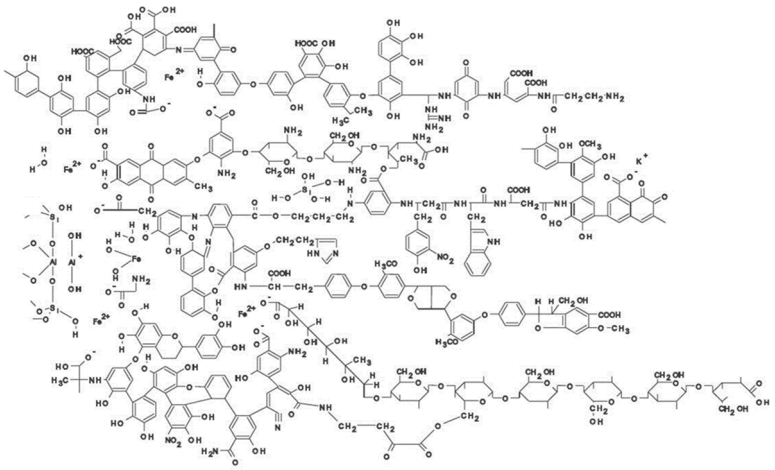


Fig. 3. Hypothetical structure of soil humic substances.

The main forms of silica in solution are considered to be:

- orthosilicic acid (OSA), which, depending on the properties it exhibits in this case, can be referred to as both H_4SiO_4 and silicon tetrahydroxide $Si(OH)_4$;
- polysilicic acid (oligomers) with molecular weight up to 100 kDa and particle size up to 5 nm;
- colloidal silica with a molecular weight greater than 100 kDa and a particle size greater than 5 nm.

The boundary between oligomers and colloids is arbitrary and based on general observations - below it, polymers are usually unstable due to the process of gelation or particle growth.

Dissolution and precipitation of silica in water involves chemical reactions of hydration and dehydration catalysed by hydroxyl ions:

$$(SiO_2)_x + 2H_2O \xleftrightarrow{hydration/dehidration} (SiO_2)_{x-1} + Si(OH)_4 \quad (1)$$

Therefore, the solubility of silica in water depends on the composition of the bottom phase and is determined by the heat of hydration: at 25°C over partially hydrated amorphous silica

it is 100÷130 mg/L (depending on the degree of hydration), over anhydrous amorphous silica (quartz glass) - 70 mg/L, while over crystalline quartz - only 6 mg/L. According to [1], the thermal effect of silica hydration reactions is equal to:

$$Si(OH)_4 = SiO_{2\,(quarts)} + 2H_2O + 22{,}84\ kJ \quad (2)$$

$$Si(OH)_4 = SiO_{2\,(amorph.)} + 2H_2O + 15{,}51\ kJ \quad (3)$$

Calculation using the Nernst equation gives silica solubility values of 0.0998 mM = 5.995 mg/L and 1.919 mM = 115.3 mg/L for equations (2) and (3), respectively, which is in good agreement with the data. As a result of the constant dissolution and redeposition reactions in natural waters, the concentration of orthosilicic acid (OSA) is almost always in the interval between these two values (on average, sea water contains 6.2 mg/L of silica, river water - 13.1 mg/L; and the maximum permissible concentration for drinking water allows its maximum content of 21.4 mg/L). But these are averaged data: it is obvious that above the surface of partially annihilated CPD saturated with silicic acid it increases up to 115 mg/L, and in clayless quartz sandstone sections it decreases to 6 mg/L (in this case the re-precipitation of silica on quartz occurs in crystalline form). The equilibrium concentration of silicic acid over silicate minerals is closer to the lower limit: for example, over montmorillonite, it is reported to be 15 mg/L. In particular, in most roll deposits of Uzbekistan, the concentration of OSA in groundwater ranges from 13 to 30 mg/L [1].

It should be noted that the solubility of OSA in molecular form practically does not depend on the pH of the medium, but in alkaline medium the solubility of silica sharply increases due to the formation of anions $H_3SiO_4^-$ (and in strongly alkaline medium - $H_2SiO_4^{2-}$; for OSA pK_{A1} -= -9.7, pK_{A2} = 11.7), and at a concentration of 100÷130 mg/L and below OSA in any pH interval is not prone to polymerisation (more precisely, polycondensation) and gel formation, and at higher concentrations in the presence of solid phase there is deposition on the substrate, and in its absence - polycondensation, the rate of which is minimal at the isoelectric point (IET) at pH=2.0÷2.2, i.e. values close enough to the isoelectric point (IEP). i.e. values close enough to pH of uranium ISL. At pH<2 the rate of polycondensation is proportional to the concentration of hydrogen cations, and at pH>2.2 - proportional to the concentration of hydroxyl anions.

In the region of IEP weakly supersaturated solutions of OSA are very stable, and even strongly supersaturated solutions begin to polymerise far from instantaneously: so, a solution with 60-fold supersaturation begins to polymerise 2-3 hours, and after a day polymerises only to the dimer - silicic acid $H_6Si_2O_7$ (SA). A solution with 17 times supersaturation polymerises 50% after one week, and a solution with three times supersaturation starts to polymerise only after one month. According to the analyses, the Loyliken PS contains 92 mg/L silica (corresponding to 197 mg/L silica), i.e. the supersaturation degree is only 1.64. This suggests that it is exclusively silica in the form of OSA and SA, especially since the standard silica analysis (reaction with ammonium molybdate reagent) determines it exclusively in these two forms.

During the uranium ISL process, sulphuric acid solutions actively interact with silicates and aluminosilicates contained in the mining ore mass (MOM), leaching metal ions from them, mainly sodium, potassium, magnesium, calcium, iron and aluminium, which pass into solution in the form of corresponding sulphates. As for silicon, its behaviour is primarily determined by the structure of these silicates. In relation to acids, silicate minerals are usually divided into three groups:

- practically insoluble (acid-resistant);
- decomposable with the formation of non-gel-like silica;
- soluble with formation of silica gel.

3 Results and discussion

Repeated attempts to relate the solubility of silicates to their composition, crystal lattice structure or its energy parameters have not led to the necessary results and have revealed only some partial relationships. In particular, it is known that feldspars belong to group 1 (stable in acid). Clay minerals belonging to layered silicates belong to the 2nd group (after dissolution of vermiculite, biotite and hydrous mica there remains a very thin white "skeleton" of silica with preservation of the lamellar form of particles; similarly, after dissolution of asbestos, fibrous silica is formed in the residue, etc.). But group silicates with isolated tetrahedrons (coffinite, as well as olivine $(MgFe)_2SiO_4$, larnite Ca_2SiO_4, monticellite $CaMgSiO_4$), as well as aluminosilicates with atomic ratio Si/Al≤2 (for example, nepheline (Na, K)$AlSiO_4$ and anorthite $Ca[Al_2Si_2O_8]$) belong to the 3rd group, and they dissolve with formation of highly supersaturated (up to 100 g/l silica) solutions of OSA, in which in the IEP region gel formation occurs only after hours and even tens of hours (Fig.1). Obviously, the relatively low silica content in the PS uranium ISL is primarily due to the fact that the content of these minerals in the mining ore mass (MOM) is low [2].

Let's consider how silica affects the uranium ISL process and subsequent processing. The main uranium minerals of roll deposits are pitchblende and coffinite, which are leached at uranium ISL by sulphuric acid in the presence of oxidant - iron (III) sulphate, according to the equations:

$$UO_{2+x} + xH_2SO_4 + (1-x)Fe_2(SO_4)_3 = UO_2SO_4 + (2-2x)FeSO_4 + xH_2O \quad (4)$$

$$U(SiO_4)_{1-x}(OH)_{4x} + Fe_2(SO_4)_3 = UO_2SO_4 + 2FeSO_4 + (1-x)H_4SiO_4 + 2xH_2O \quad (5)$$

It is obvious that the reaction (4) is not affected by the presence of OSA in the solution, but the reaction (5) is very strongly affected: according to the Le Chatelier-Brown principle, an increase in the concentration of OSA in the PSC leads to a decrease in the rate of uranium leaching from coffinite.

In this regard, it is possible that the positive effect of the presence of fulvic acids in the leach solutions was caused, among other things, by the ability of fulvic acids to bind silica into a complex and thereby reduce the degree of its activity in solution.

The most detrimental effect of silica has on anionites, accumulating in their pores and thus "poisoning" them (and if the content of silica in the ion exchanger the amount of 10% leads to a decrease in the capacity of the resin on uranium by 10%, then with an increase in the content of silica up to 19.6%, the capacity of the resin on uranium fell by 32%. The existing methods of desiliconisation lead to a significant loss of mechanical strength of resin (alkaline method) or are ineffective, providing a low percentage of resin purification from silica (fluoride method).

In cooperation with the specialists of the Navoi Mining and Metallurgical Company (NMMC JSC) we summarised the few available literature data on this issue and established some regularities of silicification processes. However, this section of applied hydrometallurgy still remains one of the least studied. First of all, the mechanism of this phenomenon is unclear, since silicification is inherent in both cation-exchange and anion-exchange materials (the latter to a greater extent). In this connection, it can be assumed that silica can be sorbed on ionites as part of sulfohumic acids (SHA), since their closest analogues - lignosulfonic acid (LSA) - are known to be sorbed on both anionites and cationites. In favour of this assumption is the fact that silica, like SHA, is able to partially desorb from the ionites, contaminating the commercial desorbate and causing problems in its processing [3].

Thus, silica has a negative effect both on the uranium ISL process itself, reducing the coffinite leaching rate, and on the subsequent processing, poisoning the ion exchanger and contaminating the commercial desorbate. Consequently, reduction of silica concentration in the uranium ISL PS is a very pressing task, and if it is most expedient to remove organics

from the PS before the sorption process due to its intensifying effect on the ISL process and then return it to the recycling sorption matrixes in order to intensify the ISL process, silica should be removed permanently (so that in case of recovery of silica-containing organics in the composition of recycling leaching solutions (RLS) the problem of its desilicification arises).

Generally accepted classification divides humic acids by their solubility in aqueous medium into insoluble humic acid, which is insoluble neither in alkalis nor in acids, and soluble humic acids, which are divided into two groups: humic acids (HA), soluble only in alkaline medium, and fulvic acids (FA), soluble in acidic, neutral and alkaline medium (sometimes a third group is distinguished from them - gimatomelanic acids (GMA), soluble in ethanol). Lignin humification proceeds in the following order:

$$lignin \rightarrow FA \rightarrow HA \rightarrow humic\ substances$$

As a result of introduction of oxygen-containing uranium-bearing groundwater into the aquifer, oxidation of CPD takes place. At the first stage, oxygen dissolved in groundwater acts as an oxidising agent (so-called aerobic oxidation). aerobic oxidation), at the second stage, after all dissolved oxygen is used up - sulphates and nitrates (anaerobic oxidation), as a result of which the so-called oxidised brown coal is formed first, and at further oxidation - water-soluble organic products (so-called aqueous humus), which are carried away by formation waters - i.e. at the end of the oxidation process the organics are completely transferred into solution (i.e. annihilated):

$$humins \rightarrow secondary\ HA \rightarrow secondary\ FA \rightarrow$$
$$\rightarrow benzene\ polycarboxylic\ acids\ (BPA), lower\ fatty\ acids\ (LFA), carbon\ dioxide$$

Although FA, as it was mentioned above, is water-soluble in a wide pH range, but its salts (fulvates) with Mg, Ca, Al, Fe, as well as complexes of FA with silicic acid are insoluble in the medium close to neutral, therefore, at uranium deposits of Uzbekistan, where the content of at least one of these components in groundwater is high enough, FA in the form of fulvates and organosilicon complexes prevail in the composition of oxidised CPD. The most active accumulator of uranium in the composition of CPD is precisely FA [4].

The main structural component of humic substances (monomeric link) is the so-called phenylpropane unit (PPU) with molecular weight 170÷200 and structure C6-C3 (Fig. 4).

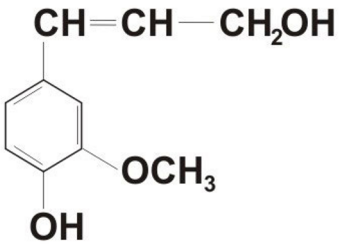


Fig. 4. Structural formula of lignin PPU.

During humification in PPU, methoxyl functional groups -OCH_3 are replaced by hydroxyl -OH (in alkaline medium) or quinoid =O (in acidic medium). During oxidation of humins to humic acids, methoxyl groups are replaced by carboxyl -COOH, and hydrogen groups by hydroxyl groups (if the substitution occurs in the benzene ring, phenolic hydroxyls -OH_{Ph} are formed, if in the propane "tail" - alcoholic hydroxyls -OH_C). As a consequence, secondary HA and FA differ essentially in composition from primary ones: their hydrogen content is essentially lower, since methoxyl groups are practically absent in their composition, but the content of carboxyls in them is essentially higher than in primary ones. Both carboxyl and phenolic hydroxyls possess ion-exchange properties, but carboxyl groups have rather strong acidic properties (pKa = 4.2÷4.8), and phenolic hydroxyls - rather weak (pKa = 8.5÷9.2),

therefore carboxyls are sorption active in a wide pH range, and phenolic hydroxyls - only in alkaline medium. The difference in the properties of HA and FA (in particular, the pH dependence of solubility) is determined by the ratio of these types of functional groups in them: HA contain 1.5÷5.7 (on average 3.6) g×eq/kg -COOH and 3.2÷7.8 (on average 5.0) g×eq/kg -OH_{Ph}, whereas FA contain 6.1÷8.5 (on average 8.2) g×eq/kg -COOH and 2.8÷5.7 (on average 3.0) g×eq/kg -OH_{Ph}. Accordingly, the insolubility of humins in water is caused precisely by its very low content of carboxyl groups [5].

The formation of sandstone deposits is associated with uranium deposition on humic acids by the chemisorption mechanism, one characteristic of which is that desorption is often impossible, and if it occurs, it is not the original substance that is desorbed, but the product of its chemical interaction with the sorbent. Thus, the interaction of HA and FA with uranyl ions occurs in two stages: at the first stage (occurring within a few seconds) uranyl ions are sorbed on carboxyls, and at the second stage (occurring within several months) there is an intra-complex reduction of uranium (6+) to uranium (4+) by phenolic hydroxyls, which are oxidised into quinoid groups, and uranium is isolated in the form of UO_2 dioxide, which gradually crystallises in the form of pitchblende or coffinite:

$$2HO-Ar-COOH+UO_2^{2+} \rightleftarrows (HO-Ar-COO)_2UO_2+2H^+ \quad (6)$$

$$(HO-Ar-COO)_2UO_2 \rightarrow (O=Ar-COO)_2U(OH)_2 \quad (7)$$

$$(O=Ar-COO)_2U(OH)_2 \rightarrow 2O=Ar-COOH+UO_2, \quad (8)$$

where Ar is the benzene (aromatic) group included in the PPU.

It is important that only uranium bound in the complex, but not remaining in solution, is reduced. Thus, the ability of humic acids to accumulate uranium is determined primarily by sorption properties rather than reductive properties - therefore, FA, inferior to HA in reductive properties, nevertheless significantly surpass them in the ability to sediment uranium.

Thus, since only uranium bound in the complex is reduced, the initial form of uranium accumulation at the gley barrier is almost exclusively non-mineral (organo-uranium): only that part of uranium that was sorbed by aqueous humus and reduced in the liquid phase is deposited in the mineral form. It should be noted that its amount can be not so low: according to the data, the average content of HA in soil solution is 1.8 g/l, and FA - 2.8 g/l (for comparison, the content of FA in it is only 6÷44 mg/L).

As already discussed, uranium (4+) formed as a result of intra-complex reduction on HA and FA is gradually isolated in the form of microscopic crystals of uranium minerals, which subsequently, as CPD annihilates, can completely replace organic matter with the formation of so-called pseudomorphoses. Due to the fact that FA actively sorb silicic acid from groundwater, in most cases CPD is replaced not by pitchblende but by coffinite due to the well-known fact that sorption of several substances at once catalyses reactions between them. Another mechanism of coffinite formation is not excluded, as described below. It is known that silica reacts with FA by different mechanisms - forming fulvates both directly with silica (acting as a base) and with metals migrating in the form of hydrosilicate complexes (both ionic and neutral):

$$R-Ar-COOH+Si(OH)_4=R-Ar-COO[Si(OH)_3]+H_2O \quad (9)$$

$$R-Ar-COOH+Ca-O-Si(OH)_3=R-COO-Ca-O-[Si(OH)_3]+H^+ \quad (10)$$

$$2R-Ar-COOH+(HO)_2Fe-O-Si(OH)_3= \\ =[R-Ar-COO]_2Fe-O-Si(OH)_3]+2H_2O, \quad (11)$$

where R is an arbitrary functional group included in the PPU.

It is known that within pH=5.5÷6.5 a considerable part of uranyl is bound in the uranylsilicate complex $UO_2SiO(OH)_3^+$ (Fig. 4). It is very likely that FA can bind this complex by the above-described mechanisms with subsequent intra-complex reduction of uranium:

$$2HO-Ar-COOH+UO_2SiO(OH)_3^+=$$

$$= (HO - Ar - COO)UO_2SiO(OH)_2(OOC - Ar - OH) + H_2O + H^+ \quad (12)$$

$$(HO - Ar - COO)UO_2SiO(OH)_2(OOC - Ar - OH) = = (O = Ar - COO)U(OH)_2 - SiO(OH)_2(OOC - Ar = O) \quad (13)$$

$$(O = Ar - COO)U(OH)_2 - SiO(OH)_2(OOC - Ar = O) = = 2O = Ar - COOh + USiO_4 + H_2O \quad (14)$$

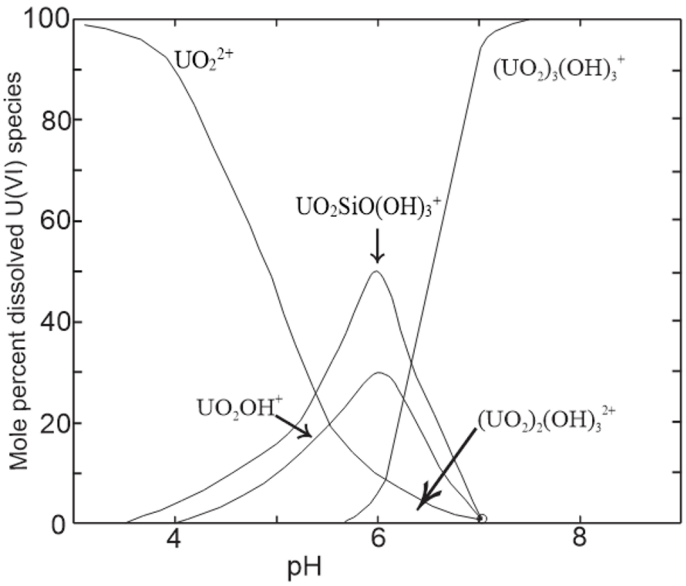


Fig. 5. pH dependence of the distribution of uranyl hydroxide and silicate complexes at 25^{0}C, and $\Sigma SiO_2 = 10^{-3}$ M and $\Sigma U = 10^{-8}$ M.

It is significant that organosilicate complexes are formed not only due to sorption of silicic acid on CPD, but also during the reverse process - during sorption of aqueous humus by hydrosilicates. In particular, aqueous humus is very effectively sorbed by clays (especially smectites) with the formation of organomineral complexes [6].

So where do organics in productive solutions during uranium ISL come from? Since HA and FA have rather strong acidic properties (for carboxyl groups, according to different authors, pK_a ranges from 2.7 to 4.8) and are effective complexing agents, many humates and fulvates do not dissociate even at pH=1.5÷2, which is typical for uranium ISL. At the same time, solubility of not only HA and FA, but also their salts strongly depends on pH: in the pH=1.5÷3.0 interval humates and fulvates of Mg, Ca, Al and Fe^{3+} pass into soluble form [7]. As for uranium, it, as mentioned above, in dissolved form and in oxidizing medium does not show a tendency to intra-complex reduction, but its complexes with HA and FA at such a low pH value dissociate to a greater extent (although not completely).

In addition, HAs in the process of ISL react significantly with sulfuric acid to form so-called sulfohumic acids (SHA) - as a result of sulfination, hydrogen groups of HA are replaced by sulfogroups $-SO_3H$, which have much stronger acidic properties than carboxylic ones (pK_A=0.31÷3.23), so sulfated HA are water-soluble even to a greater extent than FA. Suffice it to say that as a result of lignin sulfation ("initial raw material" for HA and FA, insoluble in water due to the negligible content of carboxyls), lignosulfonic acid is formed, perfectly soluble with the content of sulfogroups only 2 g × eq/kg, and forming soluble salts (lignosulfonates) not only with alkaline (as FA), but also with alkaline-earth metals.

Thus, the organics present in the uranium ISL composition is a mixture of HA, FA, SHA and their salts. Let's consider what influence these substances have on the process of ISL and the subsequent conversion processes.

At the beginning of the XXI century at the uranium deposit "Dalmatovskoye" (Kurgan region of the Russian Federation) the influence of FA as a complexing additive on the uranium ISL process was studied quite actively [8]. The authors found that in the presence of FA additives the uranium ISL process is sharply activated, uranium concentration in the PR increased by 1.5÷2.5 times, and sulphuric acid consumption decreased sharply (and the effect was especially strong at the stage of extraction). However, due to the high cost of FA ($3200/t) the expenses for reagents were not returned, and for this reason tests of lignosulfonates (LS) as their cheaper analogue were conducted, which also turned out to be quite successful. In this connection JSC "Navoi Mining and Metallurgical Combinate" commissioned Navoi State University of Mining and Technologies (NSUMT) to conduct similar studies, during which it was found that the positive effect is not due to the complexing properties of FA and LS, but to the catalytic effect of quinoid groups of FA and LS on the uranium oxidation process and increase in the filtration rate of leached solution through difficult permeable clay layers in the presence of FA and LS, at the stage of active leaching (when uranium is leached from the mineral phase) the catalytic effect is more important, and at the stage of pre-extraction (when uranium is leached mainly from sorbates on clay minerals) the effect of increasing the filtration rate of leached solution through clays comes to the fore.

For uranium ISL, the optimal solution filtration rate is considered to be in the range of 1÷10 m/day. Since the leaching rate is proportional to the square root of the filtration rate [9], a lower filtration rate significantly reduces the process rate, and a higher filtration rate reduces the uranium concentration in the PR. Consequently, to intensify uranium desorption it is desirable to increase not the total filtration rate, but only the filtration rate through clay and limonite layers, which are difficult to permeate due to the tendency to form viscous suspensions. Various reagents are widely used in drilling operations to reduce the viscosity of clay solutions, the best known of which is the so-called carbon-alkali reagent (CAR), which is a mixture of sodium humates and fulvates obtained by alkaline extraction of oxidised brown coals. Most of the other viscosity reducers are products of LS modification (ferrochrome lignosulfonate, nitrosated and chlorinated LS, etc.). It should be noted that LS affects the viscosity of $FeOOH \times H_2O$ hydrogoethite suspensions (the main component of limonite) in a similar way.

4 Conclusion

As a result of research conducted by NSUMT, various methods of LS modification were developed, which greatly increased its efficiency as an intensifier of the uranium ISL process. However, this method has not found industrial application, as it was found out that in the subsequent processing of FA has an extremely negative effect, poisoning the ionites. This is explained by the fact that HA and FA are sorbed by strongly basic anionites (this ability, for example, is used in the treatment of natural water from HA and FA), and for many ionites this sorption is only partially reversible, i.e. the sorption mechanism seems to be very different from the ion exchange mechanism. Moreover, FA sorbed on anionite are able, in turn, to sorb non-ferrous metals (in particular, Fe^{3+}), and mostly irreversibly. Thus, no more than 18% of the total amount of sorbed Fe^{3+} can be desorbed by NH_4Cl solution from fixed on anionite PCs. For this reason, it was decided to abandon the industrial introduction of FA at "Dalmatovsky".

The negative effect of FA is not limited to poisoning of the ionite: the part of FA, which is able to desorb from the ionite, during extraction causes the formation of gel-like colloidal

"interphase suspension" (the so-called "beard" or "3rd phase"). It is known that LS is reversibly sorbed on ion exchangers (both on anionites and cationites), so its use does not lead to the risk of poisoning them. However, at the stage of desorption LS will be transferred to the commercial desorbate and, as a close analogue of FA, will undoubtedly lead to the formation of "beard" during extraction. Therefore, NMMC JSC decided to refuse to use LS and its derivatives in uranium ISL.

Thus, the influence of organics on the uranium ISL process and subsequent processing is ambivalent: it intensifies the uranium ISL process very effectively, but has a very negative effect on subsequent processing (not only on ion exchange, but also on extraction). It is indicative that the experience of FA application at Dalmatovskoye showed that a particularly strong effect was observed at the pre-extraction stage. The explanation is simple: FA are effectively leached from the ore mass at the stage of acidification, and at the stage of active leaching, when the acidity of the PS is maximum, the most effective is sulphidation of HA and their removal into the PS. Thus, at this stage the PS contains a large amount of "own" FA and SHA, which actively intensify the ISL process, so the additional introduction of FAs into the composition of leaching solution has only a minor effect. At the pre-extraction stage, almost all FA and SHA have already been extracted from the ore mass, so their content in the PS is low, so the addition of FA at this stage is very effective. Since sorption matrixes are acidified in the ISL process and returned to the ISL process as circulating leaching solutions (CLS), it is obvious that the lack of FA and SHA accumulation in the CLS is caused by the fact that they are almost completely sorbed on the ionite in the sorption process and are not returned to the ISL process. For this reason, it is most expedient not just to remove organics from the PS before sorption digestion, but to return them to the recycling sorption solutions in order to intensify the ISL process.

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