

Acid-resistant liquid glass coatings using soda ash production wastes

Rena Alieva^{1*}, Zamira Mukhamedbaeva², Nargiz Olimova¹, Gaukhar Zakhiyevna³

¹Jizzakh Polytechnic Institute, Jizzakh, Uzbekistan

²Tashkent Chemical-Technological Institute, Tashkent, Uzbekistan

³M. Auezov University of South Kazakhstan, Shymkent 160012, Kazakhstan

Abstract. This article presents the results of research on the topical problems of protection of building structures, structures and products of various purposes operated in aggressive, mainly acidic environments. The existing scientific bases of obtaining high-performance acid-proof cements on the basis of liquid glass with the use of local raw materials and secondary resources of various industries are developed. Questions of increasing and improving the properties of acid-resistant liquid glass compositions by changing the input components: a primer, a filler and a hardener by introducing various active and inert additives, modifying the liquid glass, optimizing curing regimes, selection of compositions for specific operating conditions are considered.

1. Introduction

In recent years, plastic self-hardening liquid glass mixtures with calcium-containing and other substances as hardeners have been increasingly used [1,2,3]. The results of studies of processes leading to hardening of dry quartz sand and liquid glass masses when impregnated with solutions of magnesium, calcium, barium chlorides, as well as NH_4Cl and HCl , are given in the work of the authors [4,5]. Based on the unequal strength of masses impregnated with different electrolytes, and taking into account the notion that the coagulating power of cations increases with increasing cation radius, the authors come to the conclusion about the coagulation nature of hardening of masses treated with alkaline-earth metal chlorides. This point of view is confirmed by the dependence of mechanical properties of solidifying masses on the viscosity of liquid glass, with the decrease of which, with unchanged chemical composition, the strength decreases.

In another work of the authors [6] it is shown that the interaction of calcium chloride with liquid glass releases SiO_2 gel and calcium oxide adsorbing on silica gel. In dilute solutions, the interaction of concentrated sodium silicate with calcium chloride is characterized by the very rapid formation of silica film separating CaCl_2 from soluble glass. According to the authors allow the possibility of two parallel processes - adsorption of calcium oxide on SiO_2 -gel, formed due to excess against metasilicate and silica disilicate, and the formation of calcium silicate as a result of exchange reaction between CaCl_2 and silica, which is a part of meta- and sodium disilicate. The interaction of liquid glass with alkaline earth metal chlorides has also been studied by a number of other researchers. The purpose of our work is firstly: in modification of liquid sodium glass by wastes of soda production; distiller's liquid; secondly - application of new local raw materials as fillers of basalts of Karakia deposit and diabase flour of Balpantausky deposit; thirdly - modification of fillers by natural wollastonite; fourthly - on the basis of the received results of researches to make selection of compositions of acid-resistant compositions for conditions of work of chemical equipment in aggressive environments.

2. Methods

To reveal the acid resistance of the compositions under study we used the method of V.V.Moskvin [7]. Samples-cubes with a rib size of 1.41 mm were molded from plastic dough. After a day the samples were unmolded and stored for 10 days in air conditions. Acid resistance was determined in sulfuric and hydrochloric acids of concentrations - 0.5n and 5.6n, 6.1n. The solution was poured at the rate of 100 ml for each sample. In parallel, the samples were stored in tap water in closed desiccators. The solutions were replaced every two months. Compression tests were performed after

*Corresponding author: r07031965@gmail.com

28, 180, 360 days. X-ray phase analysis was performed on a modern computer-controlled diffractometer XRD-6100 (Shimadzu, Japan). CuK α radiation (β -filter, Ni, 1.54178. Current mode 30 mA and tube voltage 30 kV), constant detector rotation rate of 4 deg/min with a step of 0.02 deg were used. ($\omega/2\theta$ -coupling), and the scanning angle was varied 4 to 80o. The IR spectra of the tested samples were studied on a Nicolet I S-50 FTIRA dvanced KBr Gold spectrometer+Nicolet Continuum, manufacturer - Therma Scientific (USA).

3. Results and Discussion

To reveal the acid resistance of the compositions under study we used the method of V.V.Moskvin [7]. Samples-cubes with a rib size of 1.41 mm were molded from plastic dough. After a day the samples were unmolded and stored for 10 days in air conditions. Acid resistance was determined in sulfuric and hydrochloric acids of concentrations - 0.5n and 5.6n, 6.1n. The solution was poured at the rate of 100 ml for each sample. In parallel, the samples were stored in tap water in closed desiccators. The solutions were replaced every two months. Compression tests were performed after 28, 180, 360 days. X-ray phase analysis was performed on a modern computer-controlled diffractometer XRD-6100 (Shimadzu, Japan). CuK α radiation (β -filter, Ni, 1.54178. Current mode 30 mA and tube voltage 30 kV), constant detector rotation rate of 4 deg/min with a step of 0.02 deg were used. ($\omega/2\theta$ -coupling), and the scanning angle was varied 4 to 80o. The IR spectra of the tested samples were studied on a NicoletI S-50 FTIRA dvanced KBr Gold spectrometer+Nicolet Continuum, manufacturer - Therma Scientific (USA).

The mechanism of interaction of liquid glass with distilled liquid, sodium silicofluoride, calcium containing silicates in the presence of monomineral fine fillers is considered in the work. Distilled liquid was added as a hardener in the amount of 25, 50% of the volume of liquid glass. The chemical composition of starting materials is given in Table 1.

Table 1. Chemical composition of raw materials

Raw materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	Na ₂ O	R ₂ O	Cl	SO ₃	p.p.p.	Σ
Basalt	49.1	14.48	9.33	13.2	7.5	0.15	2.23	0.32	0.003	1.55	-	97.86
Diabase	58.28	18.27	7.39	5.32	4.70	0.001	1.74	0.10	0.05	3.51	-	99.17
wollastonite	37.22	1.00	0.80	42.83	3.95	0.07	0.1	0.19	0.06	12.50	-	98.72
Na ₂ O*SiO ₂	33.24						11.65				-	44.89
Na ₂ SiF ₆	27.9	0.10	0.12	0.30	0.30	0.01	-	31.03		0.10	-	59.86
Brine cleaning sludge	0.10	0.01	0.15	22.29	1.61	0.01	9.44		10.92	2.91	54.91	102.3

4 compositions of the following compositions were prepared:

1 composition: diabase - 63% - filler, Na₂SiF₆ - 4% - curing gas pedal, liquid glass(Na₂O-Si₂O) - 35ml.

2 composition: diabase - 56% - filler, Na₂SiF₆ - 4% - curing gas pedal, liquid glass - 35ml, wollastonite - 11%.

3 composition: Basalt - 63% - filler, Na₂SiF₆ - 4% - curing gas pedal, liquid glass - 35ml.

4 composition: Basalt - 56% - filler, wollastonite - 11%, Na₂SiF₆ - 4% - curing gas pedal, liquid glass - 30ml.

Table 2 shows the results of mechanical strength and coefficients of chemical resistance of samples of compositions of 4 compositions using liquid glass and distiller's liquid

Table 2. Mechanical strength and acid resistance coefficients of samples of acid-resistant compositions based on liquid glass and distiller liquid

Lineups	Ultimate strength of MPa specimens stored in aggressive environments and CS*				
	H ₂ O	0.5 n H ₂ SO ₄	6.1 n H ₂ SO ₄	0.5n HCl	5.6 n HCl
	28 daily hardening				
1	7.1/0.67	17.9/1.5	13.6/1.92	9.3/1.31	7.9/1.11
2	17.1/0.97	29/1.7	33.36/1.97	24.62/1.44	21.03/1.23
3	8.1/1.0	14.3/1.76	21.42/2.64	11.34/1.40	13.09/1.72
4	30.81/1.20	56.38/1.83	83.71/72	45.29/1.47	59.84/1.78
	180 daily hardening				
1	14.81/1.59	17.9/1.21	28.56/1.93	19.83/1.34	17.46/1.18
2	14.2/1.62	24.42/1.72	28.26/1.99	21.00/1.48	18.03/1.27
3	12.5/1.00	22.88/1.83	33.36/2.67	18.75/1.50	22.25/1.78
4	11.14/1.23	25.89/1.89	37.54/2.74	20.96/1.53	24.80/1.81
	360 daily hardening				
1	25.76/1.59	32.38/1.26	50.63/1.97	36.24/1.41	31.10/1.21

The results of the table show that on the basis of diabase and basalt it is possible to obtain acid-resistant cements with not very high strength indices in water and in acid solutions. At introduction of wollastonite in the composition of diabase flour mechanical strength of cement at 28 days of age increases twice. So at the composition 1 strength in water, 0,5n-sulfuric acid, 0,5n-hydrochloric acid is respectively 7,1 MPa, 10,7 MPa, 9,3 MPa. At introduction of wollastonite the mechanical strength increases and makes accordingly -17,1MPa,16,8 MPa,15,7 MPa.

When basalt flour is used as a filler, the mechanical strength of the samples is characterized by high indices. And the introduction of wollastonite in the composition of basalt flour increases the chemical resistance in water and in concentrated acid solutions. So, the strength in water from 8,1MPa increases up to 21 MPa, in 6,1 n- from 21,4 MPa to 23,7 MPa, in 5,6 n- HCl from 13,9 to 15,2MPa.

At partial replacement of liquid glass with distillery liquid solution in the amount of 25% very high results were obtained, especially at introduction of natural wollastonite into compositions 1,3. So at composition 2 strength parameters are as follows: in water-17,1 MPa; in 0,5n-H₂O 29MPa; in 6,1 H₂O 33,68 MPa, at composition 4 the following results were obtained accordingly: in water -39.88 MPa; in 0.5 n-sulfuric acid - 56.38 MPa; in 6.1 n-sulfuric acid -83.71 MPa; in 0.5 n-hydrochloric acid - 45.29 MPa and in 5.6 n-hydrochloric acid -59.84 MPa. The obtained results indicate the previously mentioned positive influence of calcium and chlorine-containing compounds on the hardening processes of acid-resistant binders based on liquid glass.

Thus, partial replacement of liquid glass with distillery liquid increases the chemical stability of samples depending on their composition. The best composition is the 4th composition based on basalt and wollastonite.

The chemical stability of the obtained diabase and basalt acid-resistant cements can be judged by the calculated resistance coefficients.

Table 2 summarizes the results of durability coefficients of 1,2,3,4 compositions based on liquid glass and distillery liquid of 28-day, 180-day and 360-day age of curing in water, in weak and concentrated solutions of hydrochloric and sulfuric acids. The data of the table show a smooth increase in the CW of all the compositions. With increasing time of operation in water and aggressive media the introduction of wollastonite gives higher resistance coefficients, especially in concentrated sulfuric and hydrochloric acids. The highest results are observed for the 4th composition. So, at 360-day curing the resistance coefficient in water is 1,25; in 0,5n-sulfuric acid -1,93; in 6,1n-sulfuric acid -2,76; in 0,5n-hydrochloric acid -1,58; in 5,6n- hydrochloric acid -1,87.

The study of adhesion ability of putties to different materials: metal, ceramics and rubber (Table 3) showed that the lowest adhesion properties have samples stored both in air-dry conditions and in acids to rubber, and the highest - to metal. Moreover, the adhesive ability of diabase-wollastonite composition in aggressive environment is higher than that of diabase composition - 2 MPa.

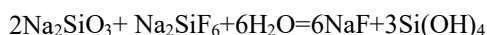
Table 3. Results of investigation of adhesion properties of diabase and diabase-wollastonite putties

Name of compositions	Materials	Tensile strength of samples, MPa, in media	
		In air	In aggressive medium
Diabase	Rubber	0,96	0,85
	Ceramic Metal	1,4	1,08
		1,93	1,145
Diabase-wollastonite	Rubber	0,99	0,87
	Ceramic Metal	2,1	1,9
		2,4	2,00

The phase composition and microstructure of liquid glass compositions based on diabase and wollastonite, basalt and wollastonite in aggressive media were investigated by complex use of physicochemical methods of analysis.

On X-ray radiographs of samples of basalt cement composition cured in 6.1n H₂SO₄ at 28-day curing many lines characteristic for minerals contained in basalt are fixed: anorthite (d=0.320; 0.269; 0.403 nm), augite (d=0.295; 0.255; 0.162 nm), anhydrous gypsum (d=0.716; 0.355 nm), sodium carbonate (d=0.253), sodium silicofluoride (d=0.334; 0.177). By 360 days, the lines of these minerals weaken, gypsum lines disappear, which indicates that it is bound in ettringite with d=0,981; 0,559; 0,466; 0,386 nm. The lines characteristic for calcium hydroxy chloride with d=0,823 nm appears.

In concentrated hydrochloric acid at 28 days of age, quartz lines d=0.445; 0.412; 0.188nm, pyroxenes d=0.312; 0.324nm intensify. NaF lines d=0.232; 0.166 nm and CaF₂ lines d=0.314; 0.193nm appear. The emerging neoplasms are in a state of high dispersibility. They confirm the complete reaction between liquid glass and sodium silicofluoride [8].



Calcium hydroxychloride crystal phase d=0.734; 0.555; 0.383 nm appears, which causes the formation of structure, providing stability of cement in aggressive media.

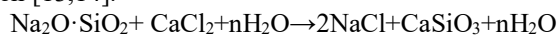
In weak acid solutions (HCl and H₂SO₄) on X-ray radiographs of samples of basalt cement composition are fixed mainly peaks characteristic for basalt flour minerals - quartz, pyroxene. Blurring of peaks speaks about formation of silicic acid gel and tobermorite gel. The high peak is characteristic of calcium hydroxychloride ($d=0.832$ nm). Modification of basalt composition with natural wollastonite indicates the intensity of diffraction maxima, diffraction lines are blurred, only at the end of the X-ray diagram appear high peaks characteristic of calcium hydrocarbonates and hydroxychlorides. In the initial terms of hardening interplanar distances characteristic for silica phases are more intense, there are lines Na₂SiF₆ $d=0,455$; $0,307$ nm, which by 360 days disappear, there are lines of villionite and fluorite, which indicate the fine crystalline structure of compositions blurred lines characterize the increase in silicic acid gels. Introduction of distiller's liquid, soda production waste leads to X-ray amorphous structure, as well as to the formation of new compounds of calcium hydrosilicates and calcium oxychlorides. Taking into account good solubility in water of calcium oxychlorides and poor calcium hydroxide, portlandite lines are fixed in the amorphous silica clusters on X-ray radiographs. The formation of crystallohydrates shifts this reaction to the right with the resultant enrichment of the liquid glass with silica and the appearance of SiO₂-gel [9].

Thus, in the process of chemical reactions in the liquid glass compositions set on the solution of soda production waste, there is a binding of alkaline cations into compounds, the composition of which is largely determined by the nature of the initial substances. The transformation of liquid glass into SiO₂-gel is caused by the formation of oxychlorides and, probably, calcium hydrochlorides, as well as sodium chloride.

The rate of hydrolysis of sodium silicofluoride slows down, but the mechanism of interaction and the nature of the formed products remain unchanged [10,11,12].

The results of tests showed high chemical stability of the samples mixed with distiller's liquid depending on its amount, as well as the type and concentration of acids. Increasing the amount of distiller's liquid up to 50% with respect to liquid glass leads to a decrease in the resistance coefficient, which probably indicates the weak crystallization ability of high-silica sodium silicates.

At contact with liquid glass of distiller's liquid an intermediate zone of whitish, turbid SiO₂-gel is instantly formed. Common in the interaction of chlorides and sodium silicofluoride with liquid glass is the zonal structure of the interaction boundary of solutions of initial substances. In the process of chemical reactions there is binding of alkali cations into compounds, the composition of which is largely determined by the nature of the initial substances. When calcium chloride interacts with liquid glass, SiO₂ gel and calcium oxide adsorbing on silica gel are released. In dilute solutions, the interaction of concentrated sodium silicate with calcium chloride is characterized by a very rapid formation of silica film separating CaCl₂ from soluble glass. In this case, two parallel processes are possible - adsorption of calcium oxide on silica gel formed due to excess silica against metasilicate and disilicate, and formation of calcium silicate as a result of exchange reaction between CaCl₂ and silica, which is a part of meta and disilicate sodium according to the total equation [13,14].



Introduction of electrolyte additives CaCl₂, NaCl into the cement dough contributes to the change of crystallization conditions of hydrate phases, increasing the degree of supersaturation of the liquid phase in relation to hydration products by increasing the ionic strength of the solution.

In the case of distiller liquid containing CaCl₂ and NaCl, the transformation of liquid glass into SiO₂-gel is caused by the formation of calcium oxychlorides and probably hydrochlorides. When the samples are kept in aggressive media, the improvement of crystallization degree of the formed phases - CaSiF₆, NaF, CaF₂ with the appearance of weak intensities of the strongest lines of calcium hydrosilicates peculiar to tobermorite Ca₅(Si₆O₁₈H₂)₄H₂O - with diffraction maxima $d = 0.307$; 0.215 ; 0.206 ; 0.200 nm is observed radiographically.

Thus, solidification of liquid-glass compositions set with distillery liquid proceeds as a result of chemical reactions of binding of alkali cations into compounds, the phase composition of which depends on the nature of initial substances. [16,17,18] X-ray diffraction patterns indicate crystalline phase formation in weak and concentrated solutions of HCl. Peaks characteristic of anorthite, augite, pyroxenes occur, which indicates incomplete decomposition of basalt. In concentrated and weak H₂SO₄ solutions, complete decomposition of basalt and wollastonite is observed. The peak characteristic for Na₂SiF₆ is absent, which confirms the complete reaction between sodium silicofluoride and liquid glass. With the increase of hardening time there appear new formations characteristic for portlandite, calcium hydrocarbonates, ettringite and calcium oxychloride. Blurred peaks are characteristic of tobermorite gels and silicic acid gels.

The composition of the formed products of interaction of liquid glass with calcium silicates can be judged by the type of IR spectroscopy curves. Fig. 1 shows IR spectra of samples of the 4th composition: basalt, wollastonite, sodium silicofluoride, liquid glass diluted with distiller's liquid, stored in water; 0.5n and 5.6n hydrochloric acid solutions. The IR spectra of the water stored samples are slightly different from the IR spectra of the samples stored in acid solutions. The strain vibration interval in the region of 790-500 cm⁻¹ has longer peaks. The sharpness of the peak of the bands

indicates an increase in the degree of crystallization of hydrate neoplasms at 785-722-648 cm⁻¹. The band at 1450-1460 cm⁻¹ is characteristic of the bonding of sodium cations with CO₂ groups. In the interval 1400-1500 falls absorption band of Ca - O bond vibration. A small band at 1430 cm⁻¹ is characteristic of the spectrum of Na₂CO₃, which indicates the presence of sodium carbonates and hydrocarbonates Na₂CO₃-n H₂O [19,20,21].

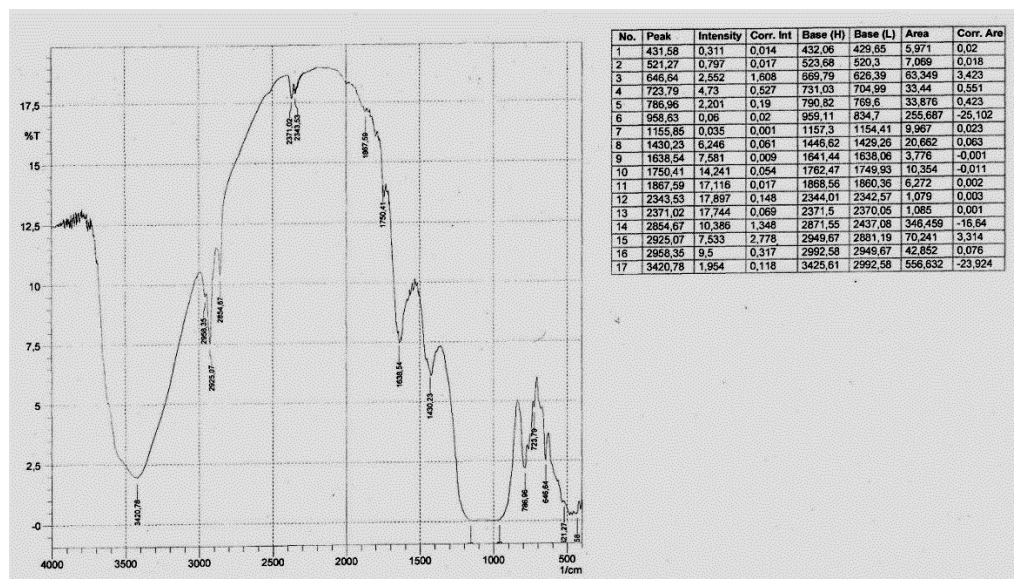


Fig. 1. IR spectra of the samples of compound 4 stored in water

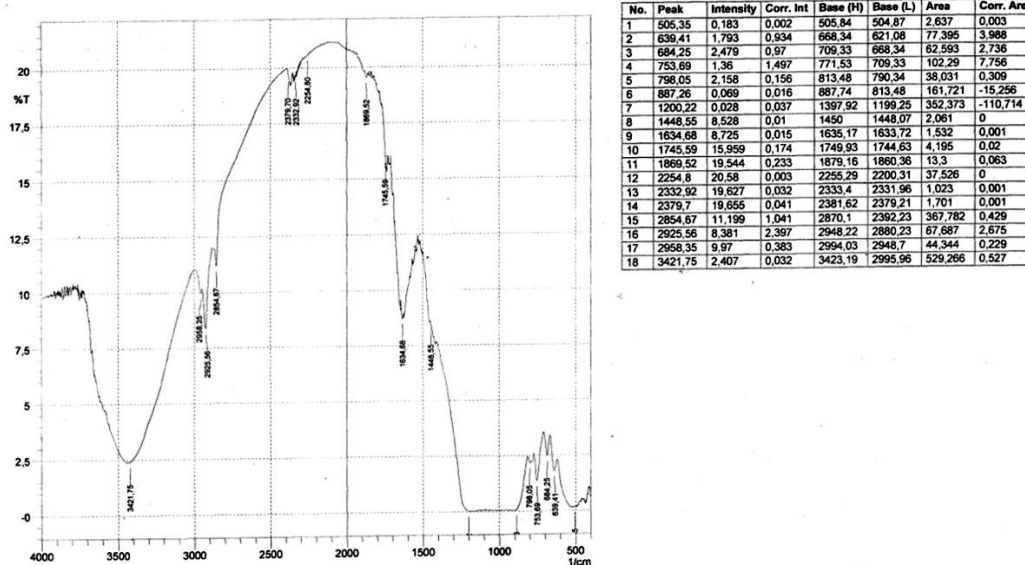


Fig. 2. IR spectra of samples of the 4th composition stored in 0.5n HCl

The spectra of the samples stored in HCl solutions are almost identical, the only difference being a more blurred band of deformation vibrations at 3500 cm⁻¹. The broad bands of vibrations of hydroxyls bound to silicon atoms at 2600-3600 cm⁻¹ probably corresponds to the band of OH vibrations of SiOH groups in the silicate of CaNaHSiO₄ composition. The broad bands show the basic vibrations of silicon and oxygen atoms of Si-O-Si in SiO₄-4 groups. Lines 785-722 indicate the presence of Al occurring as [AlO₄]-4 groups. The 1110-1000 and 500 cm⁻¹ vibrational bands found in all spectra of silicates belong to the basic vibrations of SiO₄-4, which are the elementary structural units of silica and all silicates. The band with a maximum at 1638 cm⁻¹ indicates the presence of crystallization water in liquid glass and distillers liquid - H-O-H deformation vibrations. Thus, the IR spectroscopic analysis confirms that the strengthening of the structure of the acid-resistant composition is due to chemical and intermolecular interaction of the components [22].

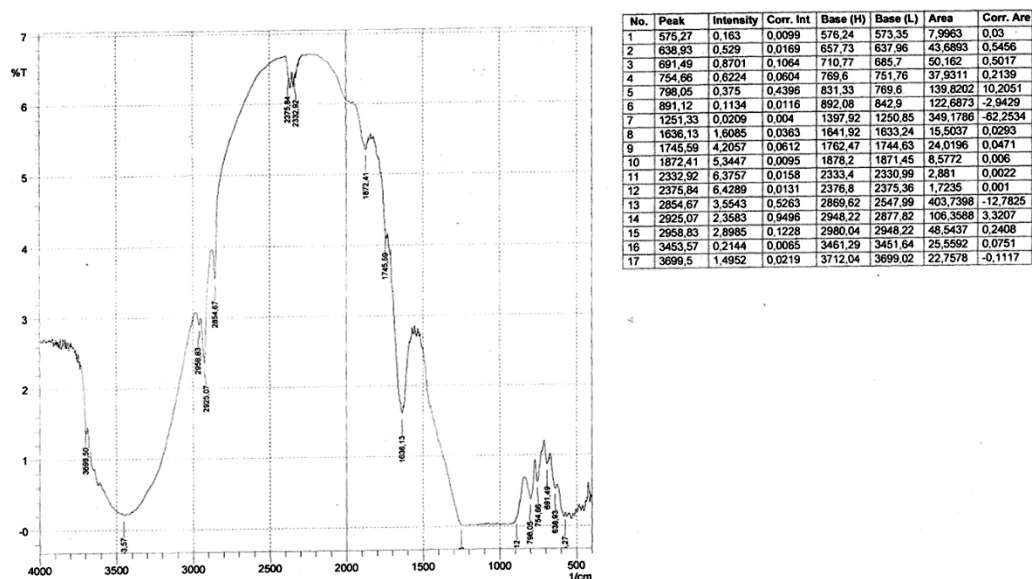


Fig. 3. IR spectra of samples of the 4th composition stored in 5.6 n HCl

4. Conclusion

On the basis of conducted research it is possible to draw a conclusion about possibility of using diabase and basalt flour as filler for acid-resistant cements, and partial replacement of liquid glass with distiller's liquid solution - waste of Kungrad soda plant considerably increases both mechanical strength of samples and chemical stability in aggressive media.

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