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Effect of Waste Polymer Additives on the Properties of Acid Resistant Composites

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ABSTRACT

The present work describes preparation of acid resistant composites from porphyrite and wollastonite by adding wastes of furfurol (PA_1) and furfuryl alcohol (PA_2) production as the polymer additives. The effects of waste polymer additives on the compressive strength, chemical resistance and adhesive ability of the composites were examined. The mechanism of the hydration process and phase evaluation of the composites were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), differential thermal analysis (DTA) and IR spectroscopy. The results indicated that hardening of the composites promoted formation of chemical bond between constituents and calcium fluoride compounds. Comparative study showed that the porphyrite composite (Sample P-2) with 1% PA_1 additive and porphyrite – wollastonite composite (Sample PW-9) with 2% PA_2 additive have optimal parameters among the samples. Acid resistance and compressive strength of prepared composites applied to surfaces of metal and ceramic materials were determined and enhanced properties of porphyrite – wollastonite composite with additive PA_2 were found to be in metal (2.4 MPa). The reason for the improvement of the chemical resistance and compressive strength of the composites may be attributed to the formation of the amorphous silicon phase.

Key Words: Porphyrite, Wollastonite, Industrial wastes, Polymer additives, Acid resistant composite.

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1. INTRODUCTION

The protection of equipments from severe chemical attacks is required in chemical, petrochemical, electrochemical and other industries. Although a number of new composites are being developed and produced, the selection of the most suitable and cost effective material for a particular application is still a difficult task.

Chemical resistant composites have been used extensively over the years to protect equipments from corrosion. It is well known that sulphate ions can react with some constituents of cement producing sulphoaluminate hydrates and gypsum, which cause expansion and/or cracking of concrete. The chemical resistance to various aggressive mediums is one of the most important properties of acid proof cement materials. The study of the chemical resistance of sulphoaluminate belite cement based on fly ash and an industrial by-product has been reported [1, 2]. It was pointed out that fly ash based sulphoaluminate belite cement is better resistant against acid, chloride and sulphate attack when compared to ordinary portland and blast-furnace slag portland cement. Generally, sulfate resistance of cement is a consequence of its mineralogical composition, mainly its low C_3A content [3, 4]. M.L.Kerr et al. [5] have reported the chemical resistance of mortars made from high alumina cement –

[♠]Corresponding author, e-mail: mirabbos_uz@yahoo.com portland cement – sand and portland cement – sand – silica fume by immersing in sulfuric acid. It was found that high alumina cement mortar and soluble glass-polyvinyl acetate modified mortar appeared to perform better compared with other mortars [6].

Polymers, which are traditionally employed for impregnated concretes, are not thermally stable enough to be used at high temperatures [7]. According to Gebauer et al. [8], polymer - cement and polymer - mortar composites showed excellent results when specimens were impregnated with monomer. In spite of a low thermal stability, polymer cement and polymer concrete are recommended for applications in aggressive mediums, e.g. floors of industrial buildings, lining structures, pickling, galvanic and electrolysis baths, and also acid and fertilizer productions [9, 10]. Furan resins are premium materials having excellent chemical resistance to acidic and basic mediums as well as to strong and polar solvents such as ketones, aromatics, and chlorinated compounds [11, 12]. Furfuryl alcohol was also used to produce a high quality polymer concrete composite and its properties were dependent on the rate of polymerization [13]. Service life of the cement composition, which was substantially free of Na and K compounds, was extended by combination of an acid resistant particulate aggregate of fused mullite, quartz and microsilica in a colloidal silica sol binder [14]. Moreover, several authors [15-20] studied hardening of the cement materials on the water glass basis. Application of polymer additives and water glass as the modifiers in cement composites has been widely studied in the past century. Modification of composite materials based on unconventional raw materials of Uzbekistan by active waste polymer additives is topical because there have been very few researches performed on it. In addition, we consider that improvement of the chemical resistance of cement composites using low cost natural raw materials and industrial wastes is potentially useful from a technical, economical and environmental point of view.

This paper describes the preparation of new sorts of highly effective acid resistant composites using unconventional raw materials of Uzbekistan – Bekabad porphyrite and Koitash wollastonite and industrial polymer wastes possessing a high compressive strength and chemical resistance in an aggressive medium and the characterization of the properties of the final products.

2. EXPERIMENTAL

2.1. Preparation of Samples

Bekabad porphyrite and Koitash wollastonite from Uzbekistan were used as the raw materials. Wastes from furfurol (PA_1) and furfuryl alcohol (PA_2) production (Fergana, Uzbekistan) were utilized as the polymer additives. Sodium fluorosilicate (Na_2SiF_2) is the waste generated during the industrial process at the Samarkand Superphosphate Plant (Samarkand, Uzbekistan). The chemical compositions of Bekabad porphyrite and Koitash wollastonite are listed in Table 1. Each dry mix of porphyrite and wollastonite was homogenized in a porcelain ball mill until complete homogeneity or 10% of residue in a number 008 sieve. The mixing of the pastes was carried out by adding water glass (35 ml), waste sodium fluorosilicate, and 0.5 to 2% of waste polymer additives PA_1 and PA_2 from weight of water glass for normal consistency. Specimens differed among themselves depending on the quantity of raw materials and industrial wastes as given in Table 2.

Table 1. Chemical compositions (mass%) of raw materials.

Oxides	Bekabad Porphyrite	Koitash Wollastonite
SiO_2	62.88	37.22
Al_2O_3	15.52	1.00
Fe_2O_3	>3.04	0.80
CaO	2.54	42.83
MgO	2.09	3.95
SO_3	0.10	-
R_2O	6.88	0.19
TiO_2	0.53	0.06
MnO	0.08	0.07
L.o.I.	4.69	12.50

Table 2. Compositions (mass%) of mixtures.

Mixture	Porphyrite, %	Na_2SiF_6, %	Wollastonite, %	Additives	
				PA_1, %	PA_2, %
P-1	90	10	-	-	0.5
P-2	90	10	-	-	1
P-3	90	10	-	-	2
PW-4	78	10	12	0.5	-
PW-5	78	10	12	1	-
PW-6	78	10	12	2	-
PW-7	78	10	12	-	0.5
PW-8	78	10	12	-	1
PW-9	78	10	12	-	2

Preparation of the pastes was completed under continuous mixing with gauging trowels for 10 min. After mixing, the paste was immediately poured into cubic moulds (20 × 20 × 20 mm) and pressed until a homogeneous specimen was obtained for testing compressive strength and chemical resistance in various aggressive mediums. The moulds were manually shaken to remove any air bubbles, and then smoothed with a spatula. For definition of adhesive ability, the paste was formed like a dumbbell in height of 78±2 mm and thickness of 23±2 mm. All specimens were preserved at room temperature (23±2ºC) for 10 days in air and then immersed into an aggressive medium for 240, 480 and 720 h, respectively. As an aggressive medium, an industrial solution of Jangiyul Hydrolysis Plant (Jangiyul, Uzbekistan) containing 1-2 % of H_2SO_4, 0.5% of HCl and 0.01% of organic impurities was used. Ten specimens were prepared from each composition. The average of those specimens was selected to investigate the influence of new local raw materials and industrial wastes on acid-proof composites. To analyze the process of acid attack, the compressive strength after immersion in an aggressive medium was examined as described in State Standard 2189-62 using a universal testing machine MIN – 100 with a capacity of 5-10 tons [21, 22].

The polished specimens were placed onto the hydraulic press to determine compressive strength and each test was conducted till its destruction under load's weight rate of 100-150 kg/min. A fixed position of an arrow on a scale at which there was a destruction of the sample. Compressive strength (σ_{CS}) can be calculated using Equation (1):

$$\sigma_{CS} = \frac{P}{F} \qquad (1)$$

where P - load under which sample collapses, MPa;

F - an area of cross-section of sample, cm.

Chemical resistance (CR) was calculated using compressive strength data of the immersed and unimmersed specimens by Equation (2):

$$\mathrm{CR}_{\mathrm{n}} = \frac{G_1}{G_2} \qquad (2)$$

where G_1 - compressive strength of the immersed specimen, MPa;

G_2 - compressive strength of the unimmersed specimen, MPa;

n – testing time.

Adhesive ability of the prepared composites was determined by testing compressive strength of composites applied to metal and ceramic [23]. Samples were kept until they hardened and then were conditioned for 7 days at 17-22°C and 70-90 % of humidity, relatively. Adhesive ability (A) of samples can be calculated using the following formula:

$$A = \frac{P}{a \cdot b} \qquad (3)$$

where P - load under which sample collapses, MPa;

a and b - size of the contact area of sample, cm.

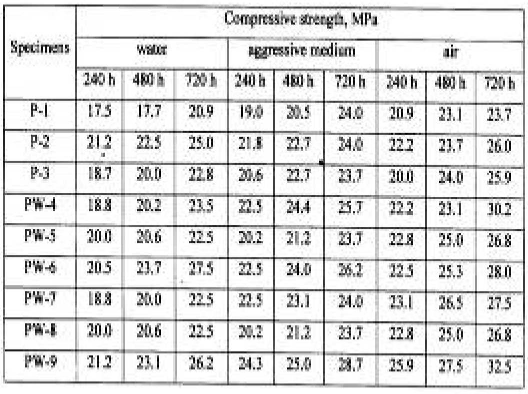
2.2. Characterization of Samples

X-ray diffraction (XRD) patterns were recorded on a DRON-2 (Russia) diffractometer using monochromated CuKα radiation to identify the crystalline phases in the samples. The thermal behaviors of the samples were studied by thermogravimetric (TG) and differential thermal analysis (DTA) using a Derivatograph Q-1500 (Hungary). The runs were carried at 20-1000°C temperature range by heating rate of 10°C/min in a dynamic atmosphere of dry air (50 ml/min). IR spectra of the composites were obtained from IR-Fourier Spectrometer (IK-20, Russia) and samples were prepared as tablets by pressing with KBr. The microstructure of the prepared samples was further examined with a scanning electron microscopy (SEM) by REM-200 (Russia) operated at an accelerating voltage of 20 kV.

3. RESULTS AND DISCUSSION

Compressive strength of the porphyrite (P) and porphyrite-wollastonite (PW) composites as a function of curing time is shown in Table 3. The chemical resistance in the specimens P-1, P-2 and P-3 increases with increasing amount of additive PA_2; the highest compressive strength being 24 to 26 MPa was found in the sample P-2. Compressive strength of the specimens PW-4 to PW-6 containing additive PA_1 is stable in the range of 25-30.2 MPa in water, aggressive medium and air, respectively, independent to the amount of additives. However, the chemical resistance of the samples using polymer additive PA_2 is relatively high compared with those of the other samples similarly prepared using additive PA_1 (Figure 1). Compressive strength is 26.2 MPa in water and 28.7 MPa in an aggressive medium for PW-9 and air stability increases up to 32.5 MPa. Probably, introducing wollastonite resulted in the increase in compressive strength of the composites (PW-4 to PW-9) both in an aggressive medium and air. Greater increased stability (32.5 MPa) in air, when kept for 720 hours, is thought to be due mainly to the addition of additive PA_2. This value varies in an aggressive medium to 28.7 MPa and in water to 26.2 MPa. Compared with the testing results of the porphyrite - wollastonite specimens, the sample PW-9 with 2% of additive PA_2 has higher characteristics. Optimum samples P-2 and PW-9 were subjected to the further step of investigation.

Table 3. Compressive strength of the porphyrite and porphyrite-wollastonite composites as a function of curing time in various mediums.



Specimens	Compressive strength, MPa								
	water			aggressive medium			air		
	240 h	480 h	720 h	240 h	480 h	720 h	240 h	480 h	720 h
P-1	17.5	17.7	20.9	19.0	20.5	24.0	20.9	23.1	23.7
P-2	21.2	22.5	25.0	21.8	22.7	24.0	22.2	23.7	26.0
P-3	18.7	20.0	22.8	20.6	22.7	23.7	20.0	24.0	25.9
PW-4	18.8	20.2	23.5	22.5	24.4	25.7	22.2	23.1	30.2
PW-5	20.0	20.6	22.5	20.2	21.2	23.7	22.8	25.0	26.8
PW-6	20.5	23.7	27.5	22.5	24.0	26.2	22.5	25.3	28.0
PW-7	18.8	20.0	22.5	22.5	23.1	24.0	23.1	26.5	27.5
PW-8	20.0	20.6	22.5	20.2	21.2	23.7	22.8	25.0	26.8
PW-9	21.2	23.1	26.2	24.3	25.0	28.7	25.9	27.5	32.5

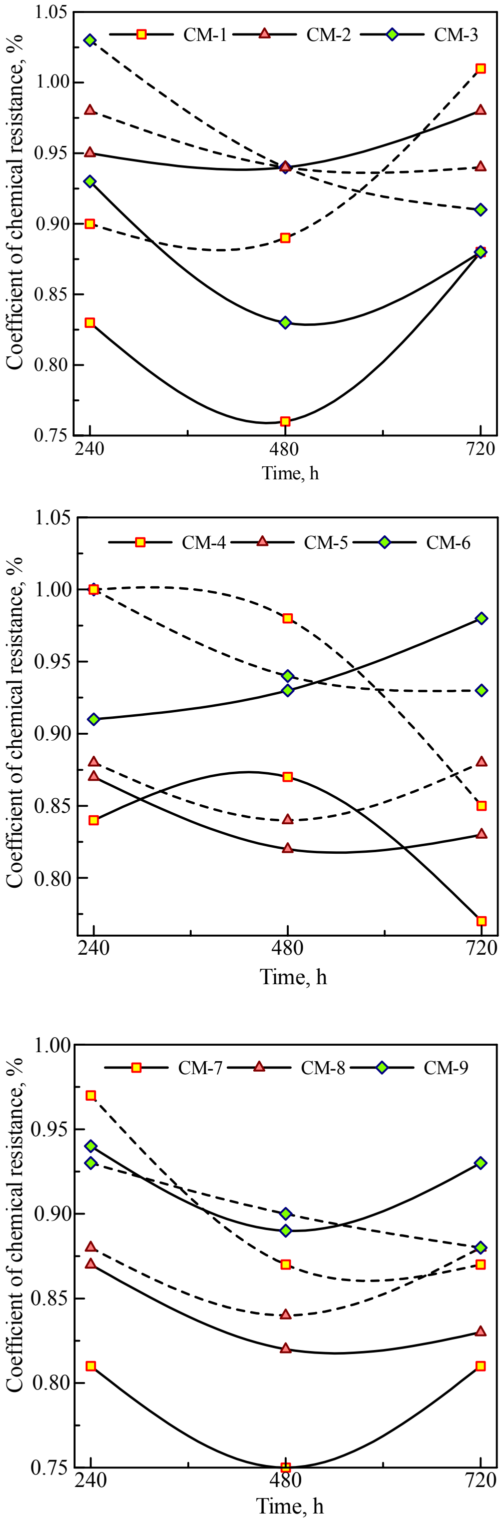
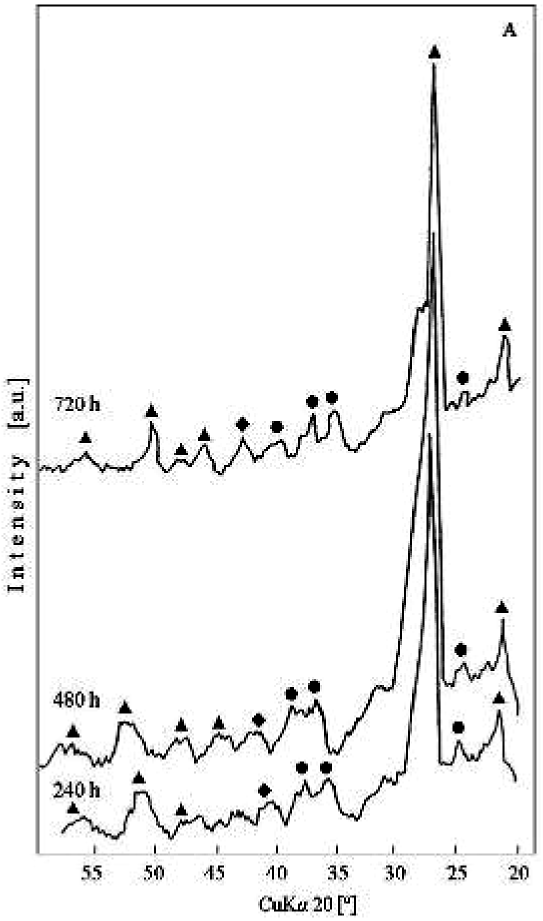


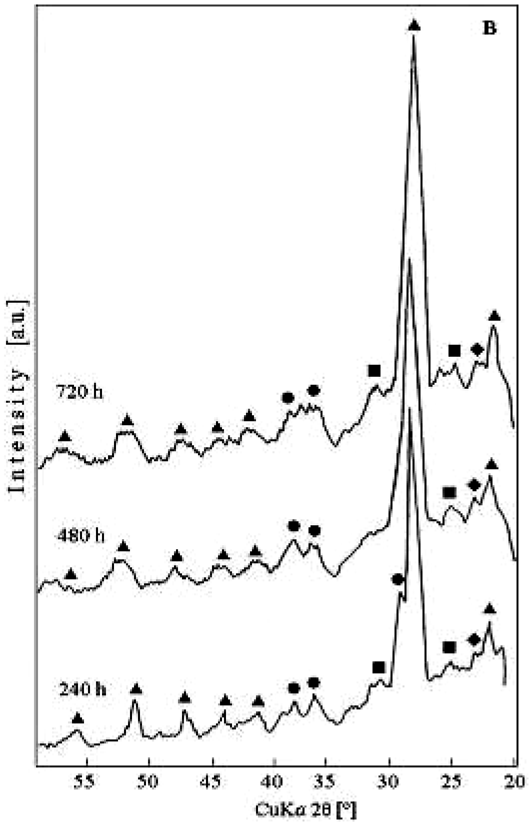
Figure 1. Chemical resistance of the porphyrite and porphyrite – wollastonite samples in water (solid line) and an aggressive medium (dashed line).

The XRD patterns (Figure 2) of the porphyrite (P-2) and porphyrite-wollastonite (PW-9) samples show the presence of quartz, albite and biotite. The intensities of these peaks are dramatically varied with increasing curing time. Formation of a new phase, ammonium sodium hydrogen phosphate $[(NH_4)NaH(PO_4)]\cdot 4H_2O$, is probably due to the reaction of the waste polymer additive PA_2 with the other constituents in the porphyrite-wollastonite samples.



(a)

Figure 2. XRD patterns of the porphyrite (a) and porphyrite-wollastonite (b) samples as a function of curing time in an aggressive medium. *Key*: (triangle): quartz; (circle): albite; (diamond): biotite; (square): $[(NH_4)NaH(PO_4)]\cdot 4H_2O$.



(b)

Figure 2 (continued). XRD patterns of the porphyrite (a) and porphyrite-wollastonite (b) samples as a function of curing time in an aggressive medium. *Key*: (triangle): quartz; (circle): albite; (diamond): biotite; (square): $[(NH_4)NaH(PO_4)]\cdot 4H_2O$.

The DTA and TG curves of the porphyrite (P-2) and porphyrite wollastonite (PW-9) are shown in Figure 3. The first endothermic peaks of these composites are observed up to 200°C and it could be attributed to the moisture removal. The deep endothermic peak at 210°C in porphyrite – wollastonite sample is ascribed to the coagulation of wollastonite with water glass. The wide exothermic peaks at 340-480°C correspond to the burn off of organics. The TG curves of samples clearly show total weight losses of 8.37 mass% in the porphyrite samples and 9.40 mass% in porphyrite – wollastonite samples in the range of 25-1000°C, respectively. These insignificant peaks, which are thought to be due to the removal of chemically bound water and dehydration of silica gel, were determined through the further heating up to about 1000°C.

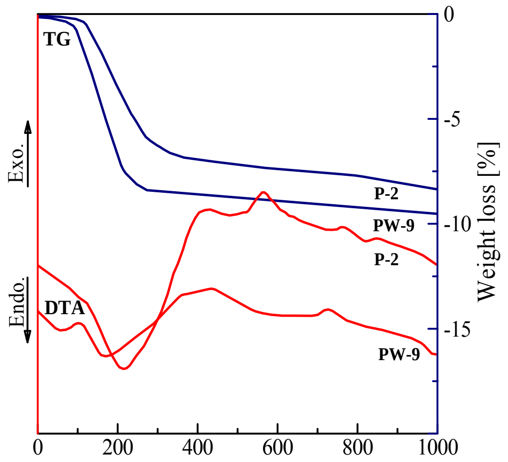
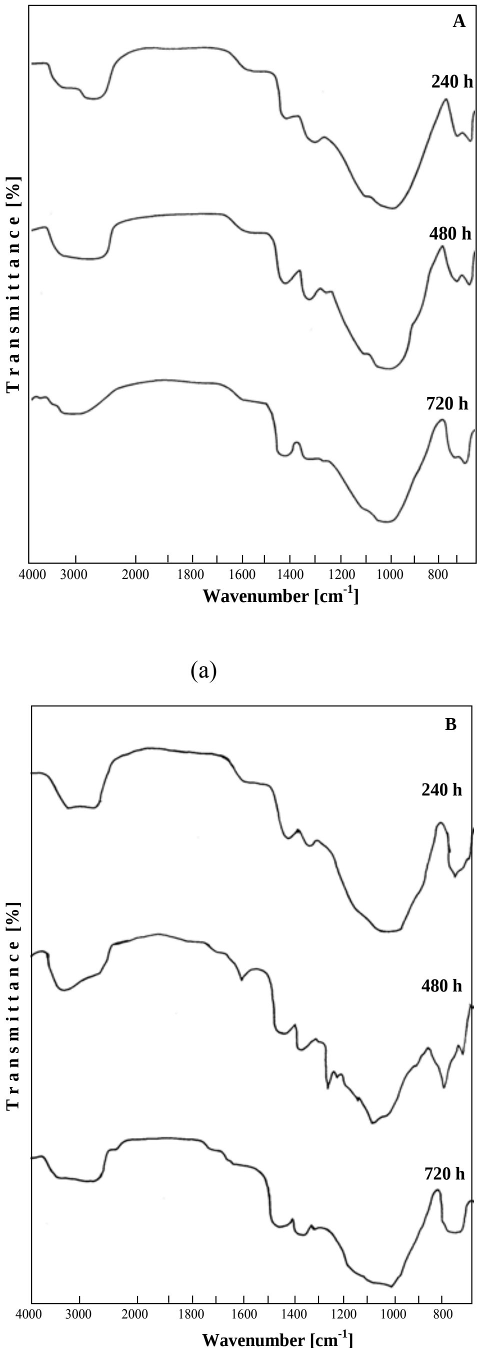


Figure 3. DTA-TG curves of the porphyrite and porphyrite – wollastonite samples.

The IR spectra of the porphyrite and porphyrite wollastonite samples are shown in Figure 4. The samples containing polymer additive PA_2 are characterized by wide stretching bands of SiO_4 tetrahedral structure at about 3000 - 2800 cm^{-1}, as well as at 1480-1380 cm^{-1} with short intensities. Increasing of adsorption bands and division of vibration frequency into two are observed in porphyrite – wollastonite samples at 1250-1000 cm^{-1}. The formed doublet is assigned to the stretching vibrations of the polymerized Si – O – Si bonds. The sharp adsorption bands testify to an increase of crystallinity in the newly formed hydrates, which have appeared during the hardening with a maximum absorption band at 1500-1430 cm^{-1}, corresponding to the breaking of deformative vibration of C = C and formation of deformative vibration of Si = Si. The adsorption band of furan (= C – O – C =) is broken off in the range of 880 cm^{-1} and new band appears at about 700-850 cm^{-1}, representing the presence of AlO_4 replaced with SiO_4.

The analysis of microstructure of prepared composites confirms above given results and characterizes the presence of crystals of quartz and albite on the light background of gel paste (Figure 5). Introducing wollastonite is very effective to further crystal formation of fluorite. A new crystal and its various habitus appeared by increasing curing time.

In this study, high compressive strength and chemical resistance of porphyrite composites in various aggressive mediums are evaluated by carrying out physico-mechanical test. Increase of the chemical resistance is probably due to a film that can prevent penetration in the internal layer of a material in an aggressive environment. Modification of the porphyrite composites by adding 12.5 % of wollastonite played the role as a stimulator for hardening. Thus, compressive strength of this porphyrite composite depended on this formed film's strength. Formation of this film is related to the mechanochemical interaction of wollastonite with an aggressive environment. XRD analysis has confirmed that hardening of the porphyrite composites is caused by formation of fluoric compounds' crystals and hydrated silica. Therefore, penetration and coefficient of diffusion of a material in an aggressive solution were sharply decreased and the corrosion process was slowed down. Probably, these phenomena may be attributed to the polymerization of superficial groups of Si – OH under high concentration of hydroxyl ions and their conversion to Si – O – Si.



(a)

(b)

Figure 4. IR spectra of the porphyrite (a) and porphyrite-wollastonite (b) samples as a function of curing time in an aggressive medium.

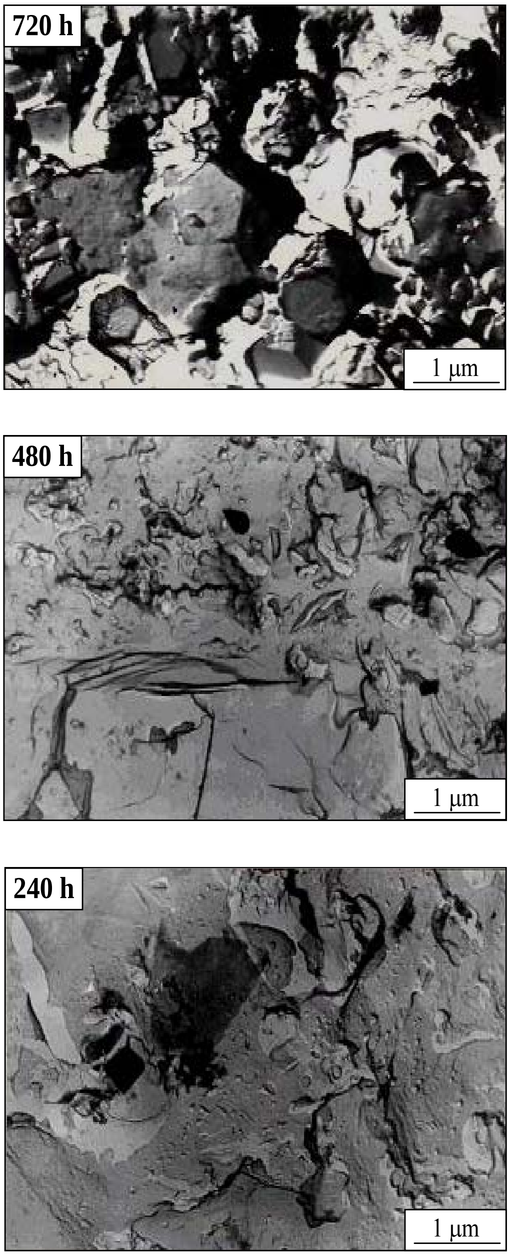


Figure 5. SEM micrographs of the porphyrite – wollastonite composite as a function of curing time in an aggressive medium.

At the interface of water glass and wollastonite, silicon leaching occurs from the solid phase surface and concentration of silicate ions increases in the solution. Increasing concentration of silicate ions in the solution favorably affects the properties of acid resistant composites.

The addition of polymeric additives, PA_1 and PA_2, increases crystallization of the samples in an aggressive medium. Crystallization proceeds faster and more completely. A strong hydration effect is an inherent in molecules of furfuryl alcohol owing to significant heat of mixture with water. Probably, hydration influence is due to hydroxyl groups of alcohol.

Structure evolution is not accompanied by initiation of solid structure of gel. A special significance to the formation period of spatial colloidal structures, which is a basis of condensation of the crystalline structures, causes higher strength. The addition of dehydrating ions of additives with water glass creates conditions for the best dispersion of porphyrite particles and strengthens the interaction between molecules of liquid paste and filler. As a result, more dispersed and homogeneous grain particles and ordered structure of the hardened composite were obtained.

High strength characteristics of the composites with additive PA_2 are due to polycondensation of the modified water glasses possessing the high adhesive ability. Investigation of adhesive ability of the composites applied to two materials – metal and ceramic- has shown that the highest compressive strength of 2.4 MPa was found in the porphyrite – wollastonite composite on metal (Table 4).

Table 4. Compressive strength of the porphyrite and porphyrite-wollastonite composites covered onto metal and ceramic.

Specimens	Material	Compressive strength, MPa	
		air	aggressive medium
P-2	Ceramic	1.40	1.08
	Metal	1.93	1.14
PW-9	Ceramic	2.10	1.90
	Metal	2.40	2.00

Acceleration of dissolution process, formation of colloidal solution and hydrating paste show the presence of salts. The presence of salts probably created conditions for soluble silica formation from a colloidal solution and dissolution entails it in the polymerization of silica. During the structure evolution, all components in the composites have contributed to the high cohesion and adhesion between them. Clearly, polymer wastes are more important for the formation of a dense impenetrable structure and strengthening of the colloidal matrix that provides high corrosive resistance to composites in an aggressive medium. Therefore, hardening of the porphyrite and porphyrite – wollastonite composites is related to the chemical and intermolecular interaction of used components.

4. CONCLUSIONS

In summary, two kinds of acid resistant composites have been prepared using Bekabad porphyrite, Koitash wollastonite and industrial wastes from furfurol (PA_1) and furfuryl alcohol (PA_2) production. Compressive strength of the specimens was stable in the range of 26-32.5 MPa in various mediums, respectively. However, the chemical resistance of the samples using waste polymer additive PA_2 was higher (1.03%) than those contained additive PA_1. Adhesive ability of the composites covered onto surfaces of metal and ceramic was determined and enhanced property of porphyrite – wollastonite composite with additive PA_2 was found to be in metal (2.4 MPa). Structure evolution was accompanied by structural transformations from amorphous - crystal to amorphous state and formation of calcium fluoride compounds. Undoubtedly, low cost and highly effective acid resistant composites offer a lot of promising benefits- like environmental and economical- for commercial purposes in the future.

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