Production and Properties of Magnesium Potassium Phosphate Cements Containing Ash and Metallurgical Slag Additives for Radioactive Waste Immobilization

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Magnesium potassium phosphate cements (MKPCs) are currently considered as the matrix materials for immobilization of radioactive waste of low and medium activity, as an alternative to Portland cements. At the same time, MKPC compound has the following advantages: fast hardening, high early strength, low shrinkage and high chemical resistance. Magnesium potassium phosphate cement is prepared at room temperature by an acid-base reaction between calcined magnesium oxide (MgO), potassium dihydrogen phosphate (KH_2PO_4) and water to form magnesium potassium phosphate hexahydrate $MgKPO_4 \cdot 6H_2O$ known as K-struvite. To obtain MKPC, starting components of high purity and, accordingly, high cost are required. From an industrial point of view, this leads to an excessive price of the final product, and therefore, the use of inexpensive industrial waste as cement fillers is economically cost effective.

In the present paper, the effect of fly ash and blast-furnace slag additives on the microstructure, compressive strength, and chemical resistance of MKPC samples was studied. The results indicate that particles of both ash and blast-furnace slag are involved in the reaction of MKPC obtaining with the formation of predominantly crystalline K-struvite. According to X-ray diffraction analysis, the content of K-struvite in samples with additives of both fly ash and blast-furnace slag is almost the same and amounts to 58–60 %. With the same addition of filler, samples with the addition of blast-furnace slag have a denser structure, which is formed due to the increased reactivity of blast-furnace slag particles. Moreover, MKPC samples with the addition of blast-furnace slag exhibit higher strength and better chemical resistance to leaching compared to MKPC samples with fly ash additions.

The obtained results demonstrate the prospects of using industrial waste additives in the production of MKPC compounds characterized by high mechanical strength and chemical resistance.

Keywords: magnesium potassium phosphate cement, fly ash, blast-furnace slag, microstructure, compressive strength, leaching.

Introduction

Recently, magnesium potassium phosphate cements (MKPC), which are formed as a result of an acid-base reaction between calcined magnesium oxide (MgO) and potassium dihydrogen phosphate (KH_2PO_4), are being considered as an alternative to Portland Cement. Compared to Portland cement, MKPC have the following advantages: fast setting, high early strength, low shrinkage, almost neutral pH, and low water requirement [1]. Magnesium potassium phosphate cements are used for a variety of applications, such as rapid repair of damaged infrastructure materials, stabilizing matrices for waste containing heavy metals, for conditioning various types of radioactive waste, for producing radiation-protective materials and dental molds with antibacterial properties [2]-[7]. Recent studies have shown that MKPC can be used for encapsulation of radioactively contaminated aluminum, which is subject to conditioning during dismantling of nuclear reactors in the process of reactor decommissioning [8].

For the practical applications of MKPC, it was proposed to use the addition of fly ash (up to 60 wt.%) in order to reduce the cost and increase the mechanical strength of the resulting composites [9]. Considering the relatively high cost of MgO and, to a lesser extent, KH_2PO_4, the use of inexpensive industrial waste and natural minerals as fillers is economically justified.

Depending on the areas of applying MKPC, various mineral additives have been proposed: sand, bentonite clay, wollastonite, metakaolin, blast-furnace slag, etc. [10]-[13]. Obviously, in such case, the characteristics of MKPC should depend on the amount of mineral additives, composition and their chemical and physical properties.

For the last 30 years, MKPC have been considered as an alternative to conventional cement when used in conditioning of radioactive waste. MKPC were developed at the Argonne National Laboratory as matrices for various nuclear waste generated during the decommissioning of old nuclear facilities in the United States [1]. Research started in the early 1990s focused on the use of MKPC to immobilize ash and salt containing radioactive waste unsuitable for cementing in conventional Portland cement mixtures.

In most cases, the original raw materials used to produce MKPC are of high purity and enough expensive. From an industrial point of view, this fact results in an excessive price per mass of the final product.

Taking into account that sand, fly ash and blast-furnace slag are commonly available and inexpensive materials in Ukraine, the use of these materials as mineral additives in the production of MKPC is quite promising. Therefore, it is of interest to study the effect of the additives on the structure, ultimate compressive strength, and chemical resistance of magnesium-potassium phosphate cements as promising matrix materials for radioactive waste immobilization.

Materials and Methods

To prepare MKPC samples with industrial waste additives, the following components were used: magnesium oxide MgO annealed at a temperature of 1300 °C, potassium dihydrogen phosphate KH_2PO_4, distilled water, fly ash from Burshtyn TPP (Thermal Power Plant, Burshtyn, Ukraine), blast furnace slag from the Mariupol Metallurgical Plant (Metallurgical plant from Mariupol, Ukraine), and sand from the Novoselivske deposit of the Kharkiv region. The initial powder components had the following characteristics:

Calcined magnesium oxide (MgO > 97 wt.%), particle size: < 200 μm

Potassium dihydrogen phosphate (KH_2PO_4 > 98 wt.%), < 630 μm

Sand (SiO_2 > 99.3 wt.%), < 400 μm

Fly ash, < 400 μm

Blast furnace slag, < 630 μm

The chemical composition of fly ash from the Burshtyn TPP and blast furnace slag from the Mariupol Metallurgical Plant is shown in Table 1.

Studying the effect of mineralogical additives on the structure and physical and mechanical properties of MKPC was carried out using cement samples of the following composition according to D. Chartier et al. [14]:

Component	Wt.%
MgO	6.47
KH_2PO_4	21.85
Sand	28.33
filler	28.33
Boric acid	0.57
Water	14.45

Table 1 – Chemical composition of the fly ash and blast furnace slag

Industrial waste	Weight content, wt. %										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	C	MnO	TiO_2	Na_2O $+K_2O$	Other components
Fly ash	46.12	18.00	22.17	4.09	1.46	0.21	2.50	0.14	1.78	2.10	1.43
Blast furnace slag	38.20	4.60	1.65	48.5	4.3	–	–	0.81	–	0.82	1.12

Fly ash and ground granulated blast-furnace slag were used as MKPC filler. In accordance with the proposed composition, mixtures for the preparation of MKPC were obtained, differing in filler: fly ash, blast furnace slag or a half of fly ash and a half of blast furnace slag. The resulting mixtures were stirred for 5–10 min until a paste-like state and placed in a cube-shaped mold with a side of 30 mm for further hardening. The temperature of the paste was raised to 43℃ and then dropped to room temperature. After removing from molds, MKPC samples were kept at room temperature. Samples of the F series with the addition of fly ash (MKPC-F), the S series with blast furnace slag (MKPC-S) and the FS series with ½ fly ash + ½ blast furnace slag (MKPC-FS) were produced.

Magnesium oxide was fired in a Nabertherm P310 high-temperature electric furnace (Germany).

To grind powders, a Pulverisette 6 planetary mono-mill (Germany) was used.

The phase composition of MKPC was studied by X-ray diffraction analysis (DRON-4-07 in copper Cu-Kα radiation using a Ni selective absorbing filter). The diffraction database ICDD PDF-2 (2004) was used for phase identification. Quantitative analysis was carried out by the Rietveld method using the MAUD software. The method is based on fitting the theoretically calculated diffractogram to the experimental one. To calculate the theoretical diffraction pattern, we used data on the crystal structure of the identified phases taken from the ICDD database.

The microstructure of MKPC samples was studied using a JSM-7001F scanning electron microscope (JEOL, Japan) equipped with a thermal field electron gun. Additionally, the images were examined in the combined mode of secondary and reflected electrons. The chemical composition of the samples was determined by energy dispersive X-ray microanalysis using an INCA Penta FETx3 analyzer (Oxford Instruments, UK).

To determine the behavior of MKPC samples during heating process, differential thermal (DTA) and thermographic (TG) analyzes were performed on an SDT Q600 V20.9 Build 20 thermal analyzer in the temperature range of 20–1000 ℃, heating rate of 10 ℃/min.

Tests for the chemical resistance of MKPC samples were carried out by leaching in distilled water at a temperature of 25 ℃.

The concentration of elements in the leachate was studied using a high resolution mass spectrometer with ionization in inductively coupled plasma ICP-MS ELEMENT 2.

Tests of MKPC samples for mechanical strength under uniaxial compression were carried out on an electromechanical press brand "ZD 10/90" (Germany).

Results and Discussion

Figure 1 presents MKPC-F, MKPC-S and MKPC-FS samples.

MKPC samples were tested for uniaxial compressive strength. During the tests, the brittle nature of the fracture of the samples was observed. The samples were split into three to five parts. The results of mechanical tests for MKPC samples are shown in Table 2. There is a tendency to increase the compressive strength when introducing blast-furnace slag into the MKPC mixture. These samples show a maximum compressive strength after 28 days of curing equal to 21.6 MPa. Samples with fly ash are characterized by the lowest strength values for all test periods - after 7, 14 and 28 days of hardening.
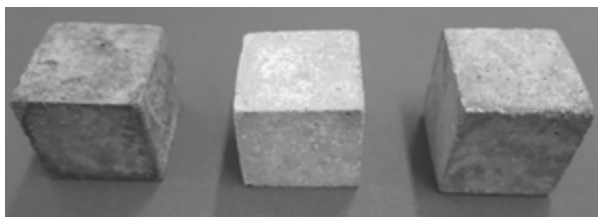

Figure 1 – MKPC-F, MKPC-S and MKPC-FS cement samples

Table 2– The compressive strength of MKPC samples

Samples	The compressive strength, MPa		
	7 days	14 days	28 days
MKPC-F	8	10	15
MKPC-S	16.5	18.8	21.6
MKPC-FS	9.6	12.8	17.2

The increase in compressive strength of samples with the addition of granulated blast furnace slag compared to samples with the addition of fly ash was observed by Gardner et al. [15]. One explanation for this fact is that the corner blast furnace slag particles can bond better to the MKPC matrix than the spherical fly ash particles. At the same time, it is emphasized that the shape of the particles is not the only reason for the differences in the mechanical characteristics of such cements.

To determine the behavior of MKPC samples during heating process, a DTA/TG analysis of cement samples MKPC-F, MKPC-S, and MKPC-FS was carried out (Figures 2b, c, d). For comparison of the obtained data, the data of DTA/TG analysis for MKPC without additives are also shown (Figure 2a) [16]. As can be seen from the figures, the position of the endothermic peak near a temperature of 120 °C, which corresponds to the beginning of K-struvite dehydration, practically is similar for these 4 cements. For MKPC samples without additives, the weight loss (~40 wt.%) on the TG curve corresponds to the loss of the stoichiometric amount of bound water. For MKPC-F, MKPC-S, and MKPC-FS, the weight loss is much less and ranges from 15.6 to 19.9 wt.% (Figures 2b, c, d). In MKPC samples without additives, weight stabilization begins at a temperature of 300°C, with additives at a temperature of 650-700 °C. This appears to be due to the decomposition and volatilization of certain compounds contained in fly ash and blast furnace slag.

To determine the durability of the obtained MKPC samples, leaching tests were carried out in distilled water at a temperature of 25 °C. The concentration of elements in the leachate solution after 1 and 14 days of leaching was determined using a high-resolution mass spectrometer with ionization in inductively coupled plasma ICP-MS ELEMENT 2.

As can be seen from Table 3, as a result of leaching in distilled water, the lowest concentrations of elements are observed in the leach solution after 1 day of leaching MKPC-S samples. The highest concentrations of elements in the leach solution are shown by the MKPC-F samples and, accordingly, the average values are shown by the MKPC-FS samples. At the same time, for all samples, the main elements of the magnesium-potassium phosphate matrix demonstrate the highest leachability: potassium, then phosphorus and magnesium. There is a high concentration of boron in the leach solution, despite its relatively small amount in the composition of MKPC. Calcium leaching is also noticeable from all three MKPC samples.

With an increase in leaching time up to 14 days, the lowest concentrations of elements are observed for the MKPC-S sample (Table 4). As well as after 1 day, according to the degree of leaching, potassium is in
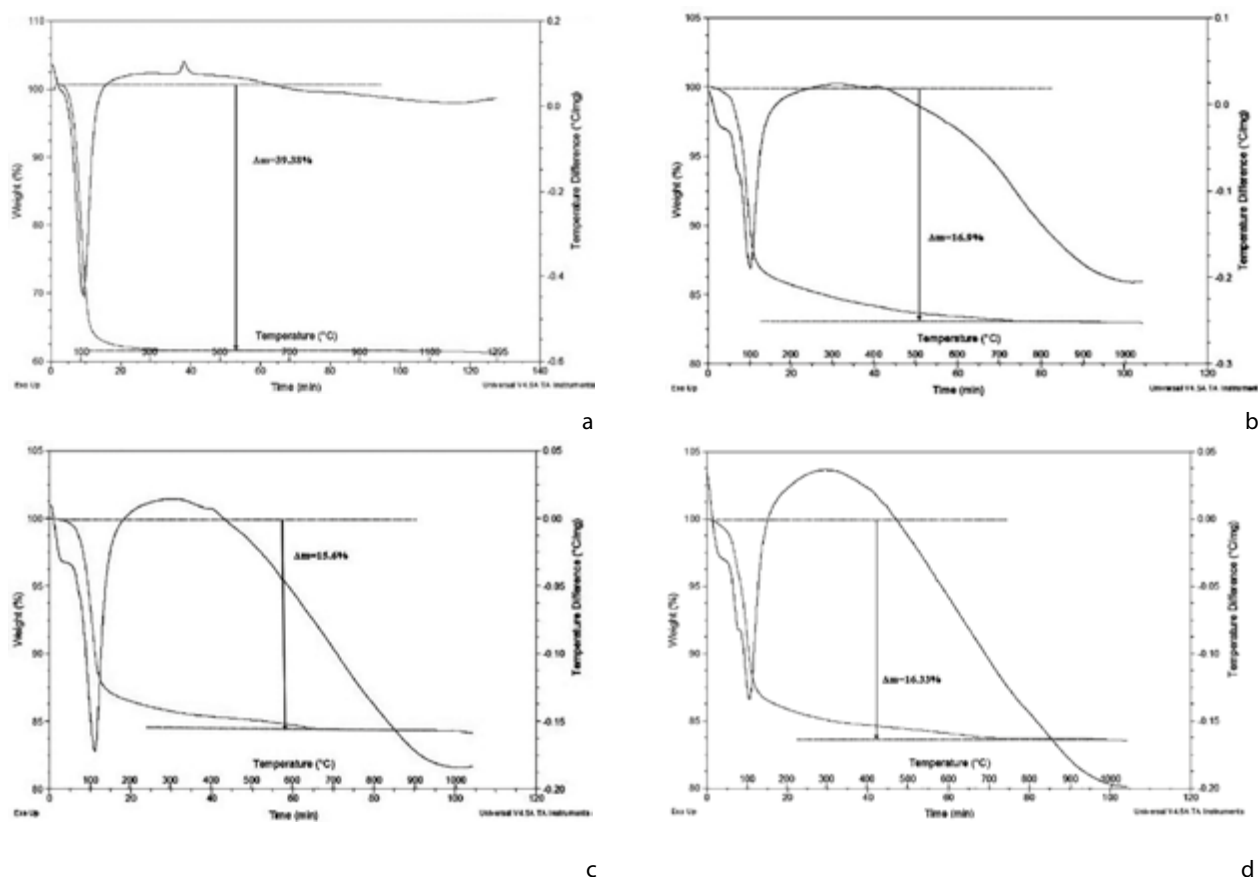
a

b

c

d

Figure 2 – DTA/TG analysis of the MKPC samples: a – MKPC without additives, b – MKPC-F, c – MKPC-S and d – MKPC-FS

Table 3 – The concentrations of elements (μg/L) in the leach solution after 1 day of leaching tests

Elements	МКРС-F	МКРС-S	МКРС-FS
Mg	26.56	13.67	13.02
K	393.50	180.12	240.45
P	91.94	44.03	52.01
B	7.91	2.83	3.67
Si	0.71	1.49	1.15
Al	0.05	0.03	0.05
Ca	3.87	3.82	2.52
Fe	0.02	0.04	0.03

Table 4 – The concentrations of elements (μg/L) in the leach solution after 14 day of leaching tests

Elements	МКРС-F	МКРС-S	МКРС-FS
Mg	36.49	15.74	20.00
K	1000.24	822.39	1386.86
P	218.51	153.64	238.18
B	25.27	16.44	21.35
Si	4.36	13.77	16.44
Al	0.05	0.07	0.04
Ca	0.00	2.10	0.00
Fe	0.01	0.02	0.02

first place, then phosphorus. It should be noted that for the MKPC-S and MKPC-FS samples, the concentrations of boron in the leach after 14 days of leaching were higher than those of magnesium. With an increase in leaching time, the concentrations of potassium, phosphorus and boron increase significantly, while the concentration of magnesium increases slightly. There is a significant increase in silicon concentration and a decrease in calcium concentration for all three MKPC samples. In addition, in contrast to 1 day leaching, the worst indicators of potassium and phosphorus leaching are observed in MKPC-FS samples.

MKPC with mineralogical additives in the form of fly ash, blast-furnace slag and sand are composite materials with K-struvite matrix. Using XRD analysis, it was found that the main phase of MKPC-F is K-struvite $MgKPO_4 \cdot 6H_2O$ (Figure 3a). The lattice parameters of the $MgKPO_4 \cdot 6H_2O$ phase are: a = 6.875Å; b = 6.160Å; c = 11.083Å. To a lesser extent, quartz SiO_2 and mullite $Al_{(4+2x)}Si_{(2-2x)}O_{(10-x)}$ are represented.

As can be seen from the presented diffraction pattern, the fly ash of the Burshtyn TPP contains quartz and mullite (Figure 3b). Moreover, a diffraction halo is presented on the diffraction pattern, which indicates the presence of an X-ray amorphous phase. The presence of quartz and mullite in MKPC-F is due to the presence of these phases in the fly ash. An increased number of X-ray lines of quartz is observed due to the presence of sand in the composition of MKPC-F.

Figure 4 shows a SEM image of the microstructure of MKPC-F samples after 28 days of curing. It can be seen that the sample material is compacted with K-struvite crystals in the form of a prism. In addition, encapsulated spherical fly ash particles and reaction products involving the fly ash are presented in the material. Apparently, the aluminosilicate glass phase of fly ash reacts in the initially acidic MKPC medium with the formation of a secondary phase, which along with K-struvite, is involved in the production of cement.

Some conclusions about the chemical activity of fly ash particles can be made on the basis of SEM energy dispersive X-ray microanalysis data. It should be noted that individual particles of fly ash powder differ significantly in chemical composition.
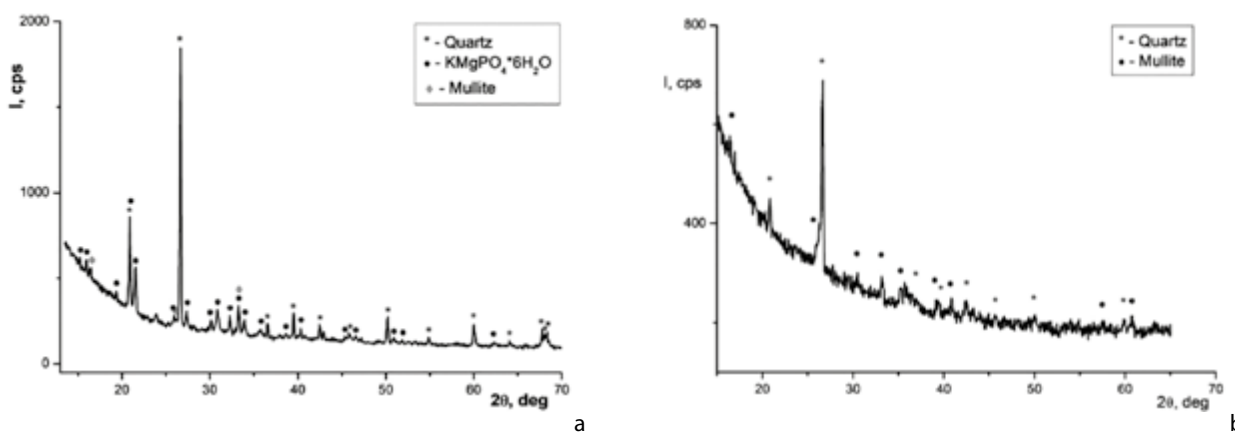

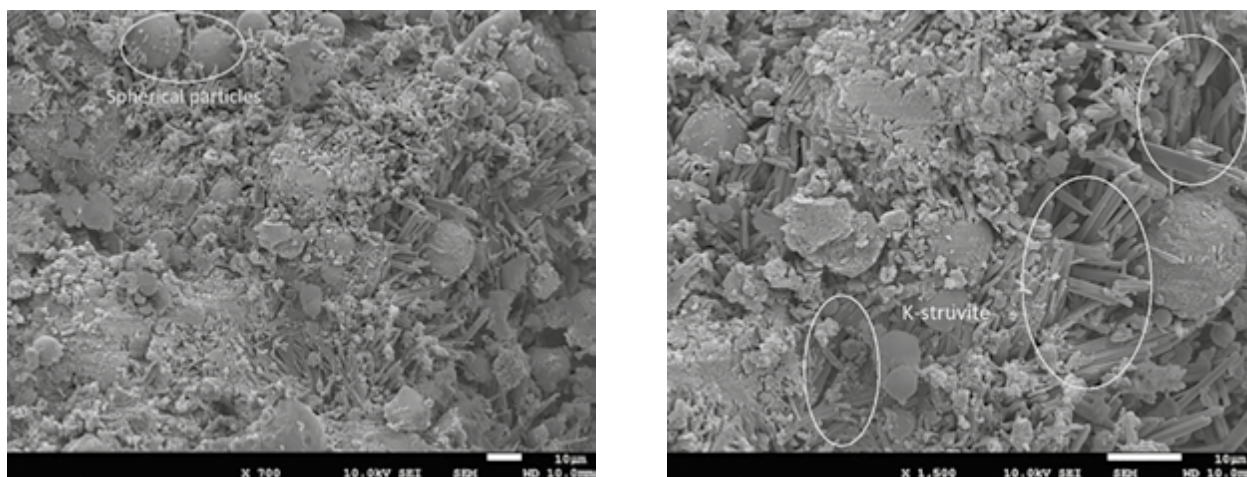Figure 3 – Diffraction patterns: a – MKPC-F, b – fly ash

Figure 4 – SEM image of the microstructure for MKPC-F samples

Previously, it was noted that fly ash particles are diverse in their chemical and mineralogical composition, and also differ in size [15], [17]. This fact results in different chemical activity of the individual fly ash powder particles. Spherical fly ash particles (area 1 in Figure 5) include the following elements: mainly Si and Al, and to a lesser extent Fe, K, Mg, Ti, Ca, and P is absent (Figure 6, Table 5). As can be seen from the maps of the element distribution, almost no Mg, K and P is observed in the place of location of the specified fly ash particle (Figures 6b, c, d). Therefore, it can be argued that such fly ash particles are not chemically active in the MKPC environment and are surrounded by needle-like K-struvite crystals and secondary reaction products.

On the contrary, another particle with shape differing from a spherical one, is characterized by increased chemical activity (area 2 in Figure 5). The increased activity of this particle is apparently due to the fact that its composition contains the maximum amount of Fe (Figure 6h, Table 5). In addition, a particle with an irregular spherical shape, which contains a significant amount of Ca in the composition, can be classified as chemically active (Figure 6g). This particle is probably a secondary product of the reaction between Ca, Al, Si with P (Figures 6d, e, f, g).

Thus, it can be argued that spherical fly ash powder particles containing elements such as iron or calcium turned out to be more reactive compared to those in which the content of Fe or Ca is very low or zero.
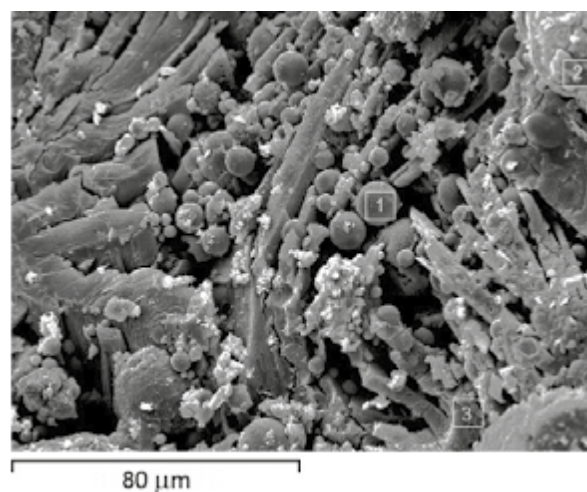

Figure 5 – SEM image of MKPC-F microstructure
for EDX analysis

Arun S. Wagh et al. [9] noted that calcium, which is represented by oxide, reacts in the same way as MgO, forms phosphate bonds, and promotes the formation of calcium-phosphate cements. It was also reported that Al and Si were incorporated into the MKPC matrix due to the dissolution of the aluminosilicate glassy fraction contained in the fly ash, which led to the formation of the potassium aluminosilicate phosphates phase [15].

Table 5 – Elemental composition of particles in the MKPC-F composition

Elements, Wt. %	O	Mg	Al	Si	P	K	Ca	Ti	Fe	Total
Area 1	34.17	1.38	20.56	32.78	-	5.32	0.57	1.18	4.04	100.00
Area 2	44.45	4.24	-	8.57	2.62	9.12	0.58	-	30.42	100.00
Area 3	50.84	7.57	5.36	9.92	9.97	12.64	1.34	-	2.36	100.00

a)

MgKa1_2 b)

K Ka1 c)

P Ka1 d)
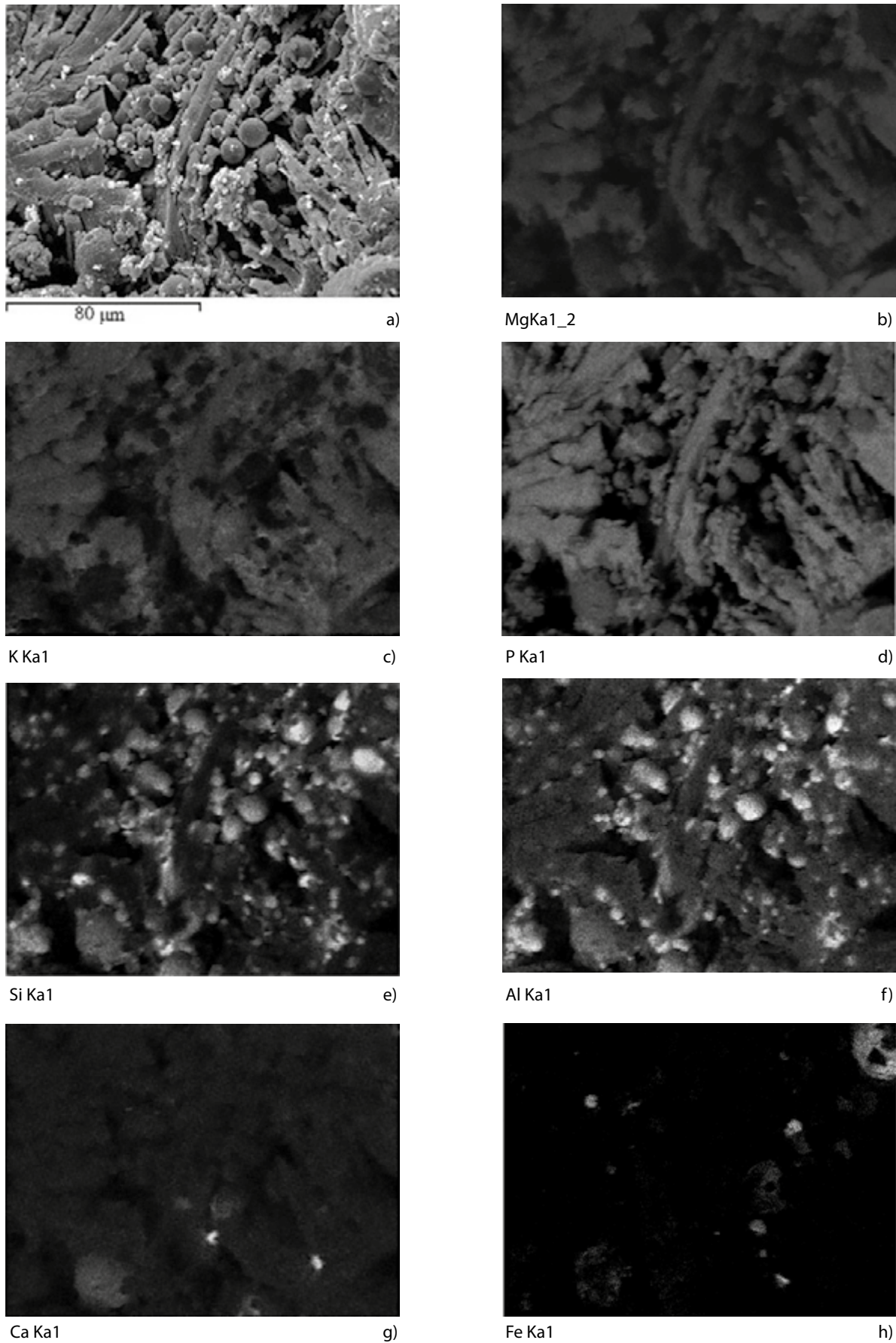
Si Ka1 e)

Al Ka1 f)

Ca Ka1 g)

Fe Ka1 h)

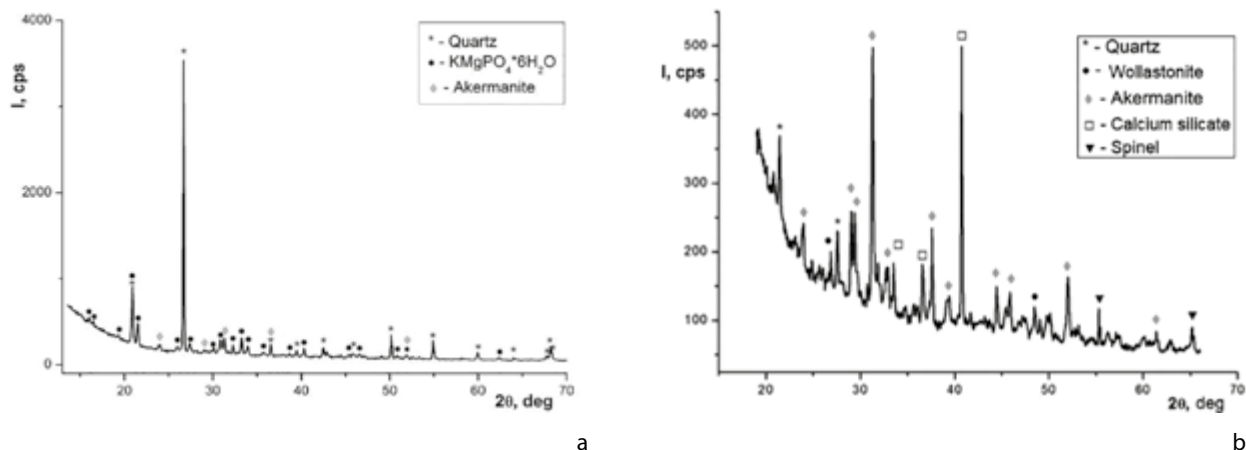Figure 6 – Maps of element distribution in the MKPC-F microstructure

Figure 7 – Diffraction patterns: a – MKPC -S, b – the slag of the Mariupol plant

Furthermore, there is an accumulation of a large number of prismatic K-struvite crystals (area 3 in Figure 5, Table 5). These crystals contain small amounts of Al and Si as well. As can be seen from the Figure 5, K-struvite crystals are formed in large pores or voids, which was also noted by Liwu Mo et al. [13].

Three phases were identified in the MKPC-S sample according to XRD analysis (Figure 7a): K-struvite $MgKPO_4 \cdot 6H_2O$, quartz SiO_2 and akermanite $Ca_2MgSi_2O_7$. The lattice parameters of the K-struvite phase for this compound are the following: a = 6.897Å; b = 6.188Å; c = 11.109Å.

The slag of the Mariupol plant is characterized by the presence of the following main phases: akermanite $Ca_2MgSi_2O_7$, as well as wollastonite $CaSiO_3$ and dicalcium silicate Ca_2SiO_4 (Figure 7b). Magnesium aluminum spinel $MgAl_2O_4$ and quartz SiO_2 are observed to a lesser extent. On the diffraction pattern of blast-furnace slag, as well as on the diffraction pattern of fly ash, there is a small diffraction halo, which indicates the presence of the X-ray amorphous phase. A part of the phases, observed in blast-furnace slag,

disappears in the diffraction pattern of the MKPC-S due to the participation in the formation of MKPC-S. Only lines of akermanite and quartz enhanced by the addition of sand to the MKPC composition remain. It should be noted that the lattice parameters of the synthesized K-struvite, as the main phase of MKPC-S, are increased compared to K-struvite MKPC-F. This indicates that in the process of preparation of MKPC-S, a more significant dissolution of blast-furnace slag particles occurs with the release of various elements and included in crystal structure of K-struvite with an increase in its lattice parameters.

SEM image of the microstructure of the MKPC-S samples after 28 days of curing is shown in Figure 8. In general, MKPC-S samples have a denser structure compared to MKPC-F samples. The structure is more uniform. Crystals of K-struvite in the form of a well-cut prism are also observed, however, they are observed less in contrast to the MKPC-F. Spherical particles practically are not observed. The presence of microcracks in the photo of the structure is caused by dehydration of the sample in vacuum during SEM.
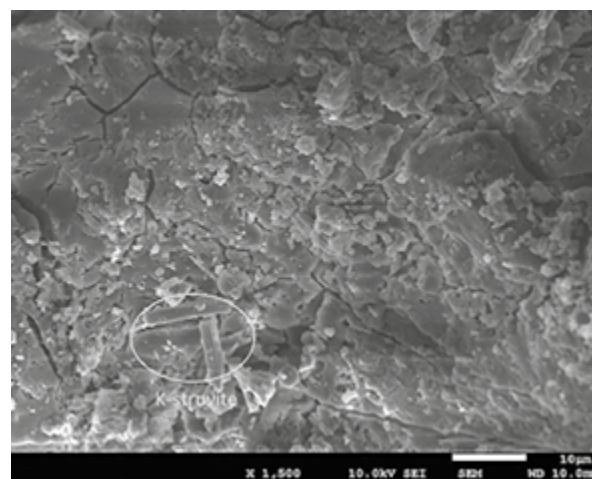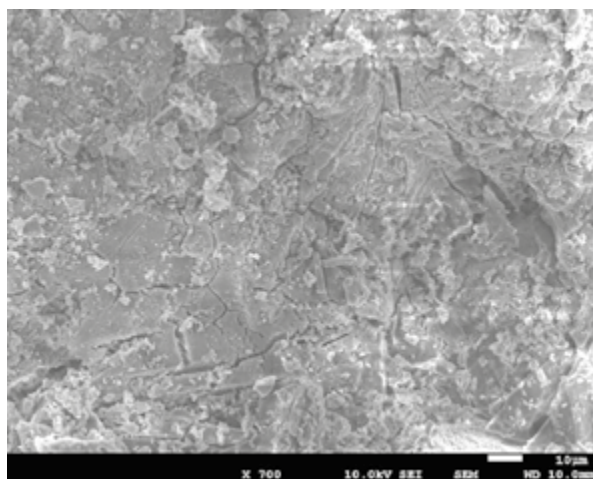

Figure 8 – SEM image of the MKPC-S microstructure.

Table 6 – Elemental composition in the dotted regions of the MKPC-S sample microstructure

Elements, Wt.%	O	Mg	Al	Si	P	K	Ca	Ti	Fe	Total
Area 1	50.15	2.62	0.08	14.61	4.03	4.69	23.53	-	0.29	100.00
Area 2	45.54	8.10	3.47	7.24	12.59	18.80	1.74	-	2.52	100.00

To compare the data of energy-dispersive X-ray microanalysis for the selected areas of the cleavage of the MKPC-S sample (Figure 9, Table 6), it is easy to notice the difference in elemental composition. Region 1 is enriched in Ca and Si. Thus, calcium silicates are concentrated in this area, which are partially dissolved in the initial acidic medium. Region 2 is characterized by the presence of Si and Al in significant amounts in addition to Mg, K, and P.

The presence of a large amount of potassium, which is located both in area 2 (Figure 9, Table 6) should be noted. A certain amount of potassium is involved in the synthesis of K-struvite (Figures 10b, c, d), while another part is involved in the secondary products enriched by Al and Si (Figures 10b, c, d, e, f). The formation of additional phases, including the secondary phase of potassium aluminosilicate phosphates, can increase the overall compaction and potentially increase the chemical resistance of MKPC [15].

Three phases were identified in MKPC-FS (Figure 11): K-struvite $MgKPO_4 \cdot 6H_2O$, quartz SiO_2, and akermanite $Ca_2MgSi_2O_7$. The lattice parameters of the $MgKPO_4 \cdot 6H_2O$ phase are: a = 6.874Å; b = 6.158Å; c = 11.091Å.

Processing of XRD analysis data using the MAUD program for samples MKPC-F, MKPC-S, and MKPC-FS shows that the content of K-struvite in all three cements is almost the same and is equal to 58-60 % (Table 7). In MKPC-S, the content of K-struvite is slightly higher than in other cements. In addition, MKPC-S is characterized by the presence of K-struvite
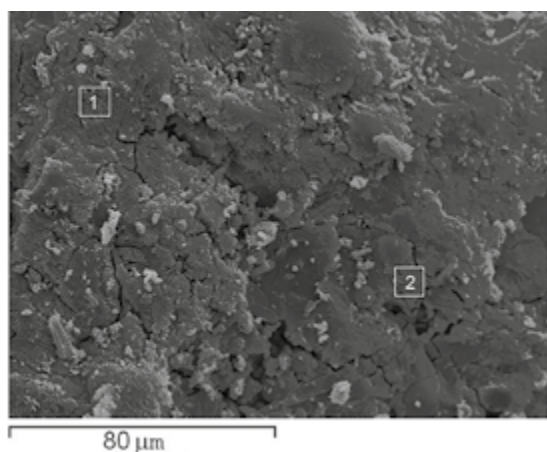
$MgKPO_4 \cdot 6H_2O$ with the highest crystal lattice parameters in comparison with both MKPC-F and MKPC-FS.

The SEM image of the MKPC-FS microstructure (Figure 12) clearly shows prism-shaped K-struvite crystals and a large amount of lamellar secondary reaction products involving particles of fly ash powder and blast-furnace slag. Compared to MKPC-F microstructure, the microstructure of MKPC-FS is more complex and denser. However, it is inferior in density to the microstructure of MKPC-S sample. There is a large number of unreacted spherical particles of fly ash and voids around these particles.

Table 7 – Phase composition of MKPC samples

No.	Phase	Weight content, % wt	Lattice parameters, Å
MKPC-F	Quartz	38	a=4,912; c=5,398
	$MgKPO_4 \cdot 6H_2O$	58	a=6,875; b=6,160; c=11,083
	Mullite	4	a=7,583; b=7,650; c=2,886
MKPC-S	Quartz	31	a=4,913; c=5,414
	$MgKPO_4 \cdot 6H_2O$	60	a=6,897; b=6,188; c=11,109
	Akermanite	9	a=7,783; c=5,028
MKPC-FS	Quartz	34	a=4,913; c=5,402
	$MgKPO_4 \cdot 6H_2O$	59	a=6,874; b=6,158; c=11,091
	Akermanite	7	a=7,773; c=5,020

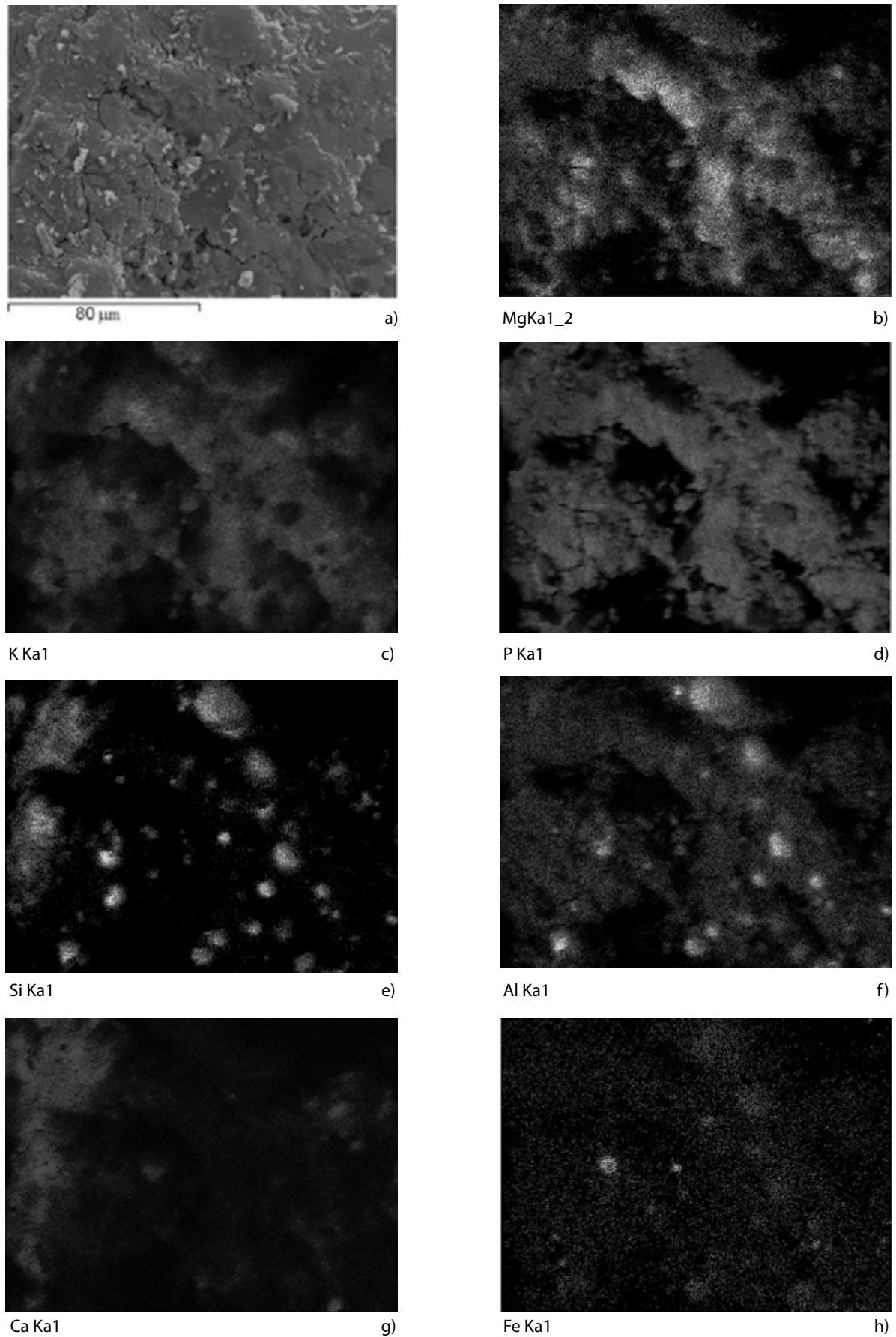Figure 9 – SEM image of the MKPC-S microstructure for EDX analysis

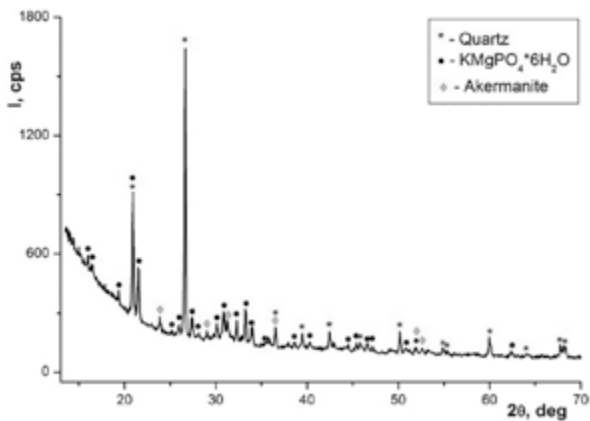Figure 10 – Maps of element distribution in the MKPC-S microstructure
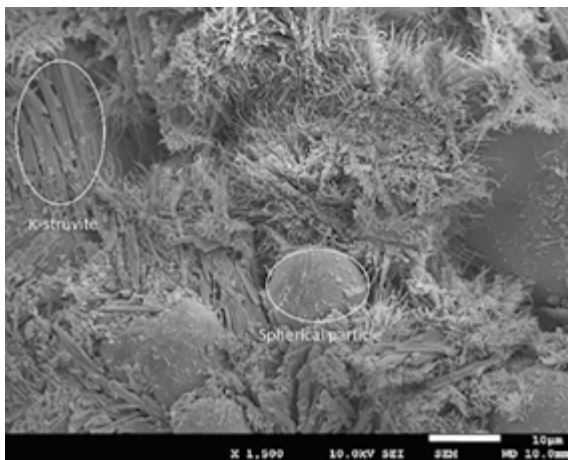
Figure 11 – Diffraction pattern of MKPC-FS

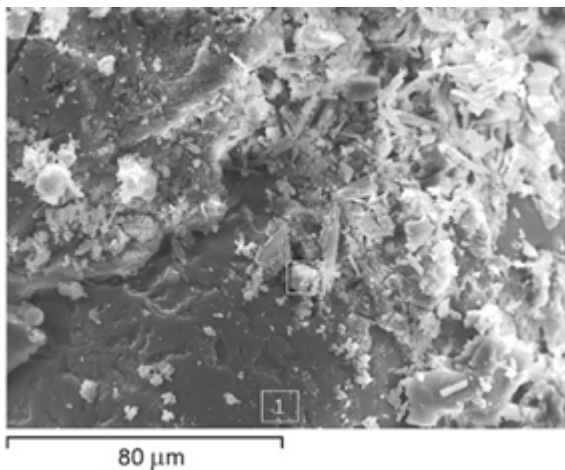Figure 12 – SEM image of the MKPC-FS microstructure

Figure 13 – SEM image of the MKPC-FS microstructure for EDX analysis

SEM/EDX analysis showed a uniform distribution of Mg, K and P, which confirms the formation of K-struvite throughout the MKPC-FS matrix (see Figures 14 a-d). It can be seen that Area 1 corresponds to unreacted sand particle (see Figure 14 e and Table 8). Area 2 corresponds to K-struvite (see Figures 14 b-d) and secondary reaction products on the base of Si, Ca and Fe (see Figure 14e, g, h and Table 8).

In contrast to unreacted fly ash particles in MKPC-F, a sand particle in MKPC-FS is quite densely surrounded by K-struvite and secondary products of the reaction with calcium (Figure 13, Table 8, Figures 14b, c, d, g).

Based on the analysis for the structural data of MKPC samples, the following conclusion can be suggested for the improvement in the mechanical strength and corrosion resistance of MKPC-S samples compared to MKPC-F and MKPC-FS samples. MKPC-F samples with the addition of fly ash as a filler are characterized by less dense compared to samples with the addition of blast-furnace slag - MKPC-S and MKPC-FS. As it was shown, some of the spherical particles of fly ash, which do not contain calcium and iron in their composition, do not react in an acidic environment. In the voids at the place of unreacted particle location, K-struvite crystals are grown, partially filling the voids (Figure 5).

In contrast to fly ash, blast-furnace slag particles are characterized by increased reactivity in an acidic environment at the initial moment of MKPC formation. This is also evidenced by the absence of most of the phases that were present in the original slag in the composition of MKPC-S: calcium silicate ($CaSiO_3$, Ca_2SiO_4) and magnesium-containing ($MgAl_2O_4$). Some elements of these compounds are entered in the crystal structure of K-struvite, as indicated by the expansion of its crystal lattice parameters (Table 7). The rest, apparently, became a part of the formed secondary phases, which are involved in the process of production of a dense homogeneous MKPC structure with the addition of blast-furnace slag. Due to the formation of a dense structure, MKPC-S samples show the best results in terms of compressive strength and corrosion resistance.

The increase in leaching of phosphorus and potassium in the MKPC-FS sample after 14 days of leaching (Table 4) can be associated with the presence of a small amount of unreacted KH_2PO_4. Unreacted KH_2PO_4 remains in the pores of the material and, since its solubility is quite high, it is washed out when exposed to water, leaving open bound pores. Then, with an increase in the total porosity and pH, a part of $MgKPO_4 \cdot 6H_2O$ (K-struvite) can also dissolve [18].

Table 8 – Elemental composition in the dotted regions of the MKPC-FS sample microstructure

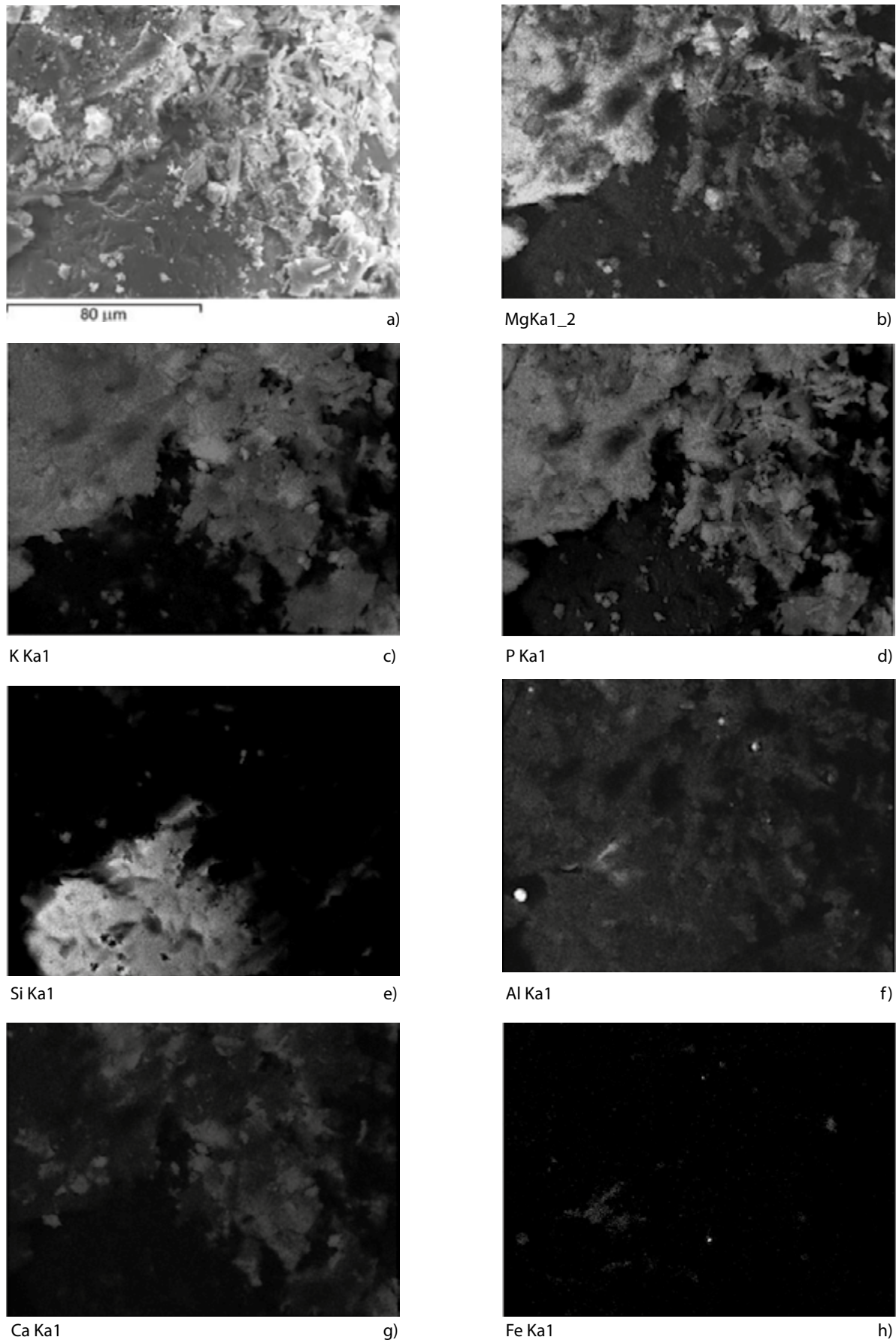| Elements, wt. %	O	Mg	Al	Si	P	K	Ca	Ti	Fe	Total
Spectrum 4	36.99	0.64	-	59.59	-	2.37	0.41	-	-	100.00
Spectrum 5	49.85	10.75	-	4.31	16.23	16.89	1.71	-	0.26	100.00

Figure 14 – Maps of elements distribution in the MKPC-FS microstructure

Conclusions

The phase composition and microstructure of MKPC were studied using fly ash, blast-furnace slag and their mixtures (50 to 50%) as fillers. These studies have shown that the content of the K-struvite main phase in all three samples is almost the same and is about 58-60 wt.%. Other phases, in addition to quartz, are mullite in MKPC with the addition of fly ash and akermanite in MKPC with the addition of blast-furnace slag. In the structure of MKPC with the addition of fly ash, unreacted spherical particles of fly ash were found. The structure of such cement is less dense compared to MKPC with the addition of blast-furnace slag.

The results of the compressive strength test showed that the maximum compressive strength of 21.6 MPa is demonstrated by MKPC samples using blast-furnace slag as a filler after 28 days of exposure.

As a result of leaching in distilled water, the lowest concentrations of elements are observed in the leach solution after 1 and 14 days of leaching MKPC samples with the addition of blast-furnace slag. MKPC samples with the addition of blast-furnace slag demonstrate the denser structure compared to other produced cements, which is formed due to the increased reactivity of blast-furnace slag particles relative to fly ash particles.

Therefore, it is advisable to conduct further studies, including a long-term leaching test of magnesium potassium phosphate cements as promising matrix materials for the immobilization of radioactive waste.

References

1. Wagh, A. S., (2016). Chemically bonded phosphate ceramics. Twenty-first century materials with diverse applications. Second Edition, Elsevier, 400 p. doi: 10.1016/C2014-0-02562-2.

2. Walling, S. A., Provis, J. L., (2016). Magnesia-based cements: A journey of 150 years, and cements for the future? *Chemical Reviews*, 116, 4170–4204. doi: 10.1021/acs.chemrev.5b00463.

3. Qiao, F., Chau, C. K., Li, Z. (2010). Property evaluation of magnesium phosphate cement mortar as patch repair material. *Construction and Building Materials*, 24(5), 695–700. doi: 10.1016/j.conbuildmat.2009.10.039.

4. Wagh, A. S., Sayenko, S. Y., Shkuropatenko, V. A., Tarasov, R. V., Dykiy, M. P., Svitlychniy, Y. O., Virych, V. D., Ulybkina, E. A. (2016). Experimental study on cesium immobilization in struvite structure. *Journal of Hazardous Materials*, 302, 241-249. doi: 10.1016/j.jhazmat.2015.09.049.

5. Sayenko, S. Y., Shkuropatenko, V. A., Pylypenko, O. V., Karsim, S. O., Zykova, A. V., Kutnii, D. V., Wagh, A. S. (2022). Radioactive waste immobilization of Hanford sludge in magnesium potassium phosphate ceramic forms. *Progress in Nuclear Energy*, 152, 104315. doi: 10.1016/j.pnucene.2022.104315.

6. Wagh, A. S., Sayenko, S. Y., Dovbnya, A. N., Shkuropatenko, V. A., Tarasov, R. V., Rybka, A. V., Zakharchenko, A. A. (2015). Durability and shielding performance of borated Ceramicrete coatings in beta and gamma radiation fields. *Journal of Nuclear Materials*, 462, 165-172. doi: 10.1016/j.jnucmat.2015.03.049.

7. Mestres, G., Ginebra, M. (2011). Novel magnesium phosphate cements with high early strength and antibacterial properties. *Acta Biomaterialia*, 7(4), 1853–1861. doi: 10.1016/j.actbio.2010.12.008.

8. Cau Dit Coumes, C., Lambertin, D., Lahalle, H., Antonucci, P., Cannes, C., Delpech, S. (2014). Selection of a mineral binder with potentialities for the stabilization/solidification of aluminum metal. *Journal of Nuclear Materials*, 453, 31–40. doi: 10.1016/j.jnucmat.2014.06.032.

9. Wagh, A., Jeong, S., Singh, D. (1997). High strength phosphate cement using industrial byproducts ashes. *Proc. of the 1st Int. Conf. on High Strength Concrete* (July 13—18, 1997, Kona, Hawaii). Editors: Azizinamini, A., Darwin, D. and French, C. The American Society of Civil Engineers 542—553.

10. Zhang, Y., Wang, S., Zhang, B., Hou, D., Li, H., Li, L., Wang, J., Lin, C. (2020). A preliminary investigation of the properties of potassium magnesium phosphate cement-based grouts mixed with fly ash, water glass and bentonite. *Construction and Building Materials*, 237, 117501. doi: 10.1016/j.conbuildmat.2019.117501.

11. Xu, B., Lothenbach, B., Winnefeld, F. (2020). Influence of wollastonite on hydration and properties of magnesium potassium phosphate cements. *Cement and Concrete Research*, 131, 106012. doi: 10.1016/j.cemconres.2020.106012.

12. Sayenko, S. Y., Shkuropatenko, V. A., Tarasov, R. V., Ulybkina, K. A., Litvinenko, L. M., Myronova, A. G., Kolodiy, I. V. (2017). Strengthening of potassium-magnesium-phosphate cement by adding additives of wollastonite and slag of metallurgical plants. *Scientific research on refractories and technical ceramics*, 117, 125-137. doi: 10.35857/2663-3566.117.12.

13. Mo, L., Lv, L., Deng, M., Qian, J. (2018). Influence of fly ash and metakaolin on the microstructure and compressive strength of magnesium potassium phosphate cement paste. *Cement and Concrete Research*, 111, 116-129. doi: 10.1016/j.cemconres.2018.06.003.

14. Chartier, D., Sanchez-Canet, J., Antonucci, P., Esnouf, S., Renault, J-P., Farcy, O., Lambertin, D., Parraud, S., Lamotte, H., Cau Dit Coumes, C. (2020). Behaviour of magnesium phosphate cement-based materials under gamma and alpha irradiation. *Journal of Nuclear Materials*, 541, 152411. doi: 10.1016/j.jnucmat.2020.152411.

15. Gardner, L. J., Bernal, S. A., Walling, S. A., Corkhill, C. L., Provis, J. L., Hyatt, N. C. (2015). Characterisation of magnesium potassium phosphate cements blended with fly ash and ground granulated blast furnace slag. *Cement and Concrete Research*, 74, 78–87. doi: 10.1016/j.cemconres.2015.01.015.

16. Sayenko S. Y., Wagh A. S., Shkuropatenko V. A., Bereznyak O. P., Hodyreva Y. S., Tarasov R. V., Virych V. D., Ulybkina E. A., Pylypenko O. V., Kholomeev G. O., Zykova A. V. (2017). Cesium immobilization into potassium magnesium phosphate matrix. *Problems of Atomic Science and Technology*, 4(110), 65-73.

17. Xu, B., Ma, H., Shao, H., Li, Z., Lothenbach, B. (2017). Influence of fly ash on compressive strength and micro-characteristics of magnesium potassium phosphate cement mortars. *Cement and Concrete Research*, 99, 86–94. doi: 10.1016/j.cemconres.2017.05.008.

18. Lahalle, H., Patapy, C., Glid, M., Renaudin, G., Cyr, M. (2019). Microstructural evolution/durability of magnesium phosphate cement paste over time in neutral and basic environments. *Cement and Concrete Research*, 122, 42–58. doi: 10.1016/j.cemconres.2019.04.011.

Отримання та властивості магній-калій-фосфатних цементів, що містять добавки золи та металургійного шлаку, для іммобілізації радіоактивних відходів

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Магній-калій-фосфатні цементи (МКФЦ) розглядаються зараз як матеріали матриць для іммобілізації радіоактивних відходів низької та середньої активності, як альтернатива портландцементу. Водночас МКФЦ компаунд має такі переваги: швидке твердіння, висока рання міцність, малі усадки та висока хімічна стійкість. МКФЦ одержують за кімнатної температури внаслідок кислотно-лужної реакції між обпаленим оксидом магнію (MgO), дигідрофосфатом калію (KH$_2$PO$_4$) та водою з утворенням гексагідрату фосфату магнію та калію MgKPO$_4$·6H$_2$O, відомого як К-струвіт. Для отримання МКФЦ потрібні вихідні компоненти високої чистоти та, відповідно, високої вартості. З промислового погляду, це призводить до надмірної ціни кінцевого продукту і тому використання недорогих промислових відходів, як наповнювачів цементів, є економічно виправданим.

У цій статті досліджено вплив добавок золи виносу та доменного шлаку на мікроструктуру, міцність на стиск та хімічну стійкість МКФЦ зразків. Наведені дані свідчать про те, що в реакції отримання МКФЦ беруть участь як частинки золи, так і доменного шлаку з формуванням переважно кристалічного К-струвіту. За даними рентгеноструктурного аналізу вміст К-струвіту у зразках із добавками, як золи виносу, так і доменного шлаку практично однаковий і становить 58 – 60 %. У разі однакового додавання наповнювача зразки з добавкою доменного шлаку мають більш щільнішу структуру, яка утворюється завдяки підвищеній реакційній здатності частинок доменного шлаку. Крім того, МКФЦ зразки з додаванням доменного шлаку демонструють більш високу міцність та кращу хімічну стійкість до вилуговування порівняно з МКФЦ зразками з добавками золи виносу. Отримані результати свідчать про перспективність використання добавок промислових відходів у виробництві МКФЦ компаундів, що характеризуються високими значеннями механічної міцності та хімічної стійкості.

Ключові слова: доменний шлак, зола виносу, магній-калій-фосфатний цемент, мікроструктура, міцність на стиск, вилуговування.