Plaster-based magnetite composite materials in construction

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Abstract. Calculation and experimental data demonstrate the possibility of using iron-ore concentrate of Lebedinsky Mining and Processing Plant (Lebedinsky GOK) in the production of plaster concrete. Their physical-mechanical, thermal and radiation protective properties were studied. Structurization mechanisms in plaster magnetite systems depending on the type of plaster binder, textures and the structure of plaster crystals providing for the design of composite materials with predetermined properties are suggested. Composite materials to ensure protection against X-ray radiation are obtained.

1. Introduction

At present, the search for new lost circulation materials and new binding agents for the production of composite materials that ensure protection against ionizing radiation remain critical. Materials on the basis of plaster binders (construction plaster and anhydrite binder) and iron oxides (hematite, goethite, maghemite, magnetite) present a certain interest in this respect.

Ferriferous minerals are widespread in nature, they are available, have low cost, developed specific surface and high sorption capacity, can be modified and regenerated, and are non toxic. The sorption capacity of magnetite is defined by structural oxygen atoms breaking the surface, which are partially hydrated in water and capable to absorb metal cations [1, 2]. High thermal and electrical conductivity of ferriferous lost circulation materials allows eliminating the main disadvantage of standard concrete materials caused by their low thermal conductivity that makes the removal of heat, generated in structural protection, complicated.

Plaster binders have a number of advantages compared to other types of binders. First of all, the hydration products of plaster binders contain 19–20 wt.% of water, which leaves the material at a temperature ranging within 60–200 °C. Heating of plaster materials leads to transformation of crystallization water into steam with high energy absorption that improves considerably the fire resistance of materials. Besides, this type of binding agents allows producing environmentally safe, healthy, free-cutting materials and articles [3].

New types of highly effective composite materials for the protection against ionizing radiation causes the need to improve the theory and practice of their design. The materials applied in the protection against radiation shall bear high radiation resistance and rather high gamma radiation attenuation factor, and besides, they shall have decent cost.

The given work covers these problems [4, 5] and is devoted to production of composite materials to ensure protection against X-ray radiation on the basis of plaster binders and iron-ore concentrate of Lebedinsky GOK, which is mainly composed of magnetite.
2. Materials and methods

The study was focused on the application of iron-ore concentrate (IOC) of Lebedinsky GOK as a raw material. IOC chemical composition, wt. %: Fe$_3$O$_4$ – 94–96; Fe$_2$O$_3$ – 0.5–1.0; SiO$_2$ – 2.0–4.0. IOC mineral composition, wt. %: magnetite – 94.1; hematite – 2.9; quartz – 2.4; carbonates – 0.2; silicates – 0.4. Magnetite (MG), being the main part of a concentrate, represented lightly oxidized iron ore with particle size not exceeding 35 $\mu$m. The modal particle diameter made 11.36 $\mu$m. Particle size distribution was wt. %: 0.2-1.0 $\mu$m - 1.3; 1.0-5.0 $\mu$m – 31.0; 5.0-10.0 $\mu$m – 33.0; 10.0-35.0 $\mu$m – 34.0.

Hardness was 6. Density was 5,800 kg/m$^3$. Color was black. Magnetite crystals had octahedral form. Their surface was smooth with some shagreen spots. IOC specific surface made 404-412 m$^2$/kg.

IOC zeta potential (–40 mV), and plaster 8 mV. $\rho$H of IOC water suspensions (W/S=12.5) equaled 8.1. There are two exo-effects according to DTA: the first – at 274 °C (oxidation up to maghemite) and the second - at 658 °C (oxidation up to hematite). According to X-ray diffraction analysis, IOC has reflexes similar to interplanar spaces, nm: 0.4848; 0.3909; 0.3345; 0.3126; 0.2974; 0.2536; 0.2426; 0.2099; 0.1799; 0.1720; 0.1612; 0.1479.

3. Main part

One of the ways to increase strength of low-grade plaster binders is to modify them with various microfillers. IOC of Lebedinsky GOK was studied as such filler.

AnII suspension has an alkaline reaction of environment ($\rho$H = 11.2) due to water polarization with SO$_4^{2–}$ ions [7, 8]:

$$2\text{CaSO}_4 + 2\text{H}–\text{OH} \rightarrow \text{Ca(HSO}_4)_2 + \text{Ca(OH)}_2.$$  \hspace{1cm} (1)

$\rho$H of CP lies within the interval from 5.5 to 7.5, which is equivalent to water polarization with Ca$^{2+}$ ions:

$$2(\text{CaSO}_4)·\text{H}_2\text{O} + \text{H}–\text{OH} \rightarrow (\text{CaOH})_2\text{SO}_4 + \text{H}_2\text{SO}_4.$$ \hspace{1cm} (2)

IOC of Lebedinsky GOK polarizes water with OH ion:

$$\text{Fe}_3\text{O}_4(\text{crystal.}) + 2\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3·\text{H}_2 + 2\text{OH}^-.$$ \hspace{1cm} (3)

When mixing suspensions of calcium sulfate and iron oxide, depending on acid condition of the environment, calcium ferrites, hydrated calcium ferrites and hydrated calcium sulfoferrites can be formed. Such reactions were studied on the basis of calculation of standard Gibbs free energy ($\Delta G^{\circ}_{298}$) [9, 10]. The calculations show (Tab. 1) that calcium ferrites in Ca(OH)$_2$ solutions may be formed in standard conditions. Whereas reactions Fe$_2$O$_3(\text{crystal.})$ and Fe$_3$O$_4(\text{crystal.})$ with Ca(OH)$_2(\text{crystal.})$ are less likely to happen. OH$^–$ ion, which is characterized by a small ionic radius (0.96×10–3 $\mu$m), can get into the structure of Fe$_2$O$_3(\text{crystal.})$ and strengthen its hydration. The interaction in standard conditions is not possible in neutral suspensions containing calcium sulfate and iron oxides since $\Delta G^{\circ}_{298} > 0$. Reaction 5
is possible at high temperatures since ($\Delta G^o_{chem} > 0$; $\Delta H^o_{chem} > 0$; $\Delta S^o_{chem} > 0$). Reaction 6 is impossible since ($\Delta G^o_{chem} > 0$; $\Delta H^o_{chem} > 0$; $\Delta S^o_{chem} < 0$).

According to calculations (Tab. 1), the formation of hardly soluble hydrated calcium ferrites in alkaline environment is more preferable than the formation of ferrites (reactions 1–6). With the reduction of acidity hydrated calcium ferrites are destroyed alongside with the formation of Fe(OH)$_3$, which can colmatage plaster stone pores thus improving its structure.

Table 1. Standard Gibbs free energy reaction

| N | Reaction | $\Delta G^o_{298}$ |
|---|----------|--------------------|
| 0 | $\text{Fe}_2\text{O}_3$ (crystal.) + $\text{Ca}^{2+}$ (sol) + 2OH$^-$ (sol) $\rightarrow$ Ca(FeO$_2$)$_2$ (crystal.) + 3H$_2$O (l) | –41.16 |
| 2 | $\text{Fe}_2\text{O}_3$ (crystal.) + $\text{Ca}^{2+}$ (sol) + 2OH$^-$ (sol) $\rightarrow$ Ca(FeO$_2$)$_2$ (crystal.) + FeO (crystal.) + 3H$_2$O (l) | –12.29 |
| 3 | $\text{Fe}_2\text{O}_3$ (crystal.) + Ca(OH)$_2$ (crystal.) $\rightarrow$ Ca(FeO$_2$)$_2$ (crystal.) + H$_2$O (l) | –9.76 |
| 4 | $\text{Fe}_2\text{O}_3$ (crystal.) + Ca(OH)$_2$ (crystal.) $\rightarrow$ Ca(FeO$_2$)$_2$ (crystal.) + FeO (crystal.) + H$_2$O (l) | 19.11 |
| 5 | $\text{Fe}_2\text{O}_3$ (crystal.) + $\text{Ca}^{2+}$ (sol) + H$_2$O (l) $\rightarrow$ Ca(FeO$_2$)$_2$ (crystal.) + 2H$^+$ (sol) | 118.44 |
| 6 | $\text{Fe}_2\text{O}_3$ (crystal.) + $\text{Ca}^{2+}$ (sol) $\rightarrow$ Ca(FeO$_2$)$_2$ (crystal.) + Fe$^{2+}$ (sol) | 75.83 |
| 7 | $\text{Fe}_2\text{O}_3$ (crystal.) + 4$\text{Ca}^{2+}$ (sol) + 8OH$^-$ (sol) + 9H$_2$O (l) $\rightarrow$ 4CaO·Fe$_2$O$_3$·13H$_2$O + FeO | –833.36 |
| 8 | $\text{Fe}_2\text{O}_3$ (crystal.) + 3$\text{Ca}^{2+}$ (sol) + 6OH$^-$ (sol) + 3H$_2$O (l) $\rightarrow$ 3CaO·Fe$_2$O$_3$·6H$_2$O + FeO | –442.30 |
| 9 | $\text{Fe}_2\text{O}_3$ (crystal.) + 4$\text{Ca}^{2+}$ (sol) + 8OH$^-$ (sol) + 9H$_2$O (l) $\rightarrow$ 4CaO·Fe$_2$O$_3$·13H$_2$O | –862.23 |
| 10 | $\text{Fe}_2\text{O}_3$ (crystal.) + 3$\text{Ca}^{2+}$ (sol) + 6OH$^-$ (sol) + 3H$_2$O (l) $\rightarrow$ 3CaO·Fe$_2$O$_3$·6H$_2$O | –471.17 |
| 11 | $\text{Fe}_2\text{O}_3$ (crystal.) + 4$\text{Ca}^{2+}$ (sol) + 6OH$^-$ (sol) + 9H$_2$O (l) + SO$_4^{2-}$ $\rightarrow$ 3CaO·Fe$_2$O$_3$·CaSO$_4$·12H$_2$O + FeO | –848.86 |
| 12 | $\text{Fe}_2\text{O}_3$ (crystal.) + 4$\text{Ca}^{2+}$ (sol) + 6OH$^-$ (sol) + 9H$_2$O (l) + SO$_4^{2-}$ $\rightarrow$ 3CaO·Fe$_2$O$_3$·CaSO$_4$·12H$_2$O | –877.73 |
| 13 | $\text{Fe}_2\text{O}_3$ (crystal.) + 6$\text{Ca}^{2+}$ (sol) + 6OH$^-$ (sol) + 28H$_2$O (l) + 3SO$_4^{2-}$ $\rightarrow$ 3CaO·Fe$_2$O$_3$·3CaSO$_4$·31H$_2$O + FeO | –2034.02 |
| 14 | $\text{Fe}_2\text{O}_3$ (crystal.) + 6$\text{Ca}^{2+}$ (sol) + 6OH$^-$ (sol) + 28H$_2$O (l) + 3SO$_4^{2-}$ $\rightarrow$ 3CaO·Fe$_2$O$_3$·3CaSO$_4$·31H$_2$O | –2062.90 |

Thus, it may be concluded that from the thermodynamic point, the reactions of formation of hydrated calcium ferrites and hydrated calcium sulfoferrites are possible. At the same time, these reactions also depend on kinetic factors. To check the above-mentioned assumptions, short-term (1 hour) and long-term (30 days) potentiometric study of processes within plaster-magnetite systems were performed.

It is found that IOC with a weakly alkaline reaction of the environment reduces the setting time of gypsum plaster: the initial setting decreases from 10 to 8.5 min. and the final setting - from 18 to 12.5 min. It also slightly reduces $K_{red}$ of gypsum plaster-based materials. Thus, in case of plain samples, $K_{red} = 0.408$, while pilot samples – 0.367. IOC additives increase pH of dehydrate and CP and decrease pH of AnII within initial hydration. In longer setting times, the pH of plaster-magnetite systems reduces, which serves as indirect confirmation of the fact that reactions 7–14 may take place (Tab. 1).

Long-term kinetic study showed that already in the first week, the IOC water suspensions are characterized by brown residue, which is caused by oxidation of Fe$^{2+}$ into Fe$^{3+}$ and interaction of the latter one with water molecules. Soon after, the same brown residue is formed in systems on the basis of (plaster + IOC) and (AnII + IOC). On the contrary, systems on the basis of CP and IOC are not
characterized by a brown residue even during long-term hydration. Systems on the basis of CP and IOC have the biggest solid volume.

The iron-ore concentrate of Lebedinsky GOK with alkaline reaction of the environment has considerable influence on hydroxylated solid plaster particles, thus displacing their acid-base balance, which will ultimately affect structurization of plaster stone. This is confirmed by potentiometric study.

The X-ray diffraction analysis of products formed in plaster-magnetite systems (Fig. 1) showed the presence of calcium sulfate dihydrate (reflexes in interplanar spaces, nm: 0.76283; 0.42908; 0.30737; 0.28801), magnetite (reflexes in interplanar spaces, nm: 0.2974; 0.2536) and syngenite (reflexes in interplanar spaces, nm: 0.95604; 0.5735; 0.47702; 0.31699) during activation of K$_2$SO$_4$ anhydrite.

![Figure 1. X-ray diffraction pattern of AM-30 composite material](image)

During activation of (NH$_4$)$_2$SO$_4$ anhydrite, the koktaite is formed (reflexes in interplanar spaces, nm: 0.9992; 0.5809; 0.4968; 0.3314; 0.2903). Samples on the basis of gypsum plaster (SGM-30) and anhydrite binder (AM-30) with IOC content of 30 wt. % were exposed to X-ray diffraction analysis. The formation of hydrated calcium ferrites and hydrated calcium sulfoferrites are not identified in X-ray diffraction pattern due to their insignificant quantities.

At present, the most widely spread gypsum binder is gypsum plaster. That is why the study was initially focused on G-4 gypsum plaster. Tab. 2 shows its compositions. The amount of hardening water was separately calculated for CP and IOC. As shown in Tab. 2, with the increase in the amount of IOC additive in a mix, the W/S decreases from 0.55 to 0.36 for CP and from 0.40 to 0.28 - for An II.

According to obtained results (Fig. 2 a), 10–40 wt. % of IOC may be introduced into gypsum plaster. In this interval of IOC volume, the R$_{сж}$ of a binder is stabilized being at the level of 12–13 MPa. The strength of pure gypsum plaster under the same hardening conditions makes 17 MPa, and density amounts to 1,367 kg/m$^3$. The density of filled IOC samples increases to 1,700 kg/m$^3$. Small IOC addition slightly reduces CP strength (up to 5%).

Anhydrite cement was also studied as a binder alongside with gypsum plaster in order to obtain composite materials. Hardening of materials on the basis of anhydrite cement was ensured within the steam-air medium. Similar to the previous case, the IOC volume varied from 10 to 80 wt. %.

| Material | IOC additive; % | W/S | Material | IOC additive; % | W/S |
|----------|----------------|-----|----------|----------------|-----|
| SG       | –              | 0.55| An       | –              | 0.40 |
| SGM -10  | 10             | 0.52| AM –10   | 10             | 0.37 |
| SGM -20  | 20             | 0.49| AM –20   | 20             | 0.37 |
| SGM -30  | 30             | 0.46| AM –30   | 30             | 0.35 |
The obtained data (Fig. 2 b) show that materials on the basis of anhydrite binder have higher strength properties than similar materials on the basis of gypsum plaster.

| SGM  | 40  | 0.43 | AM  | 40  | 0.34 |
|------|-----|------|-----|-----|------|
| SGM  | 50  | 0.40 | AM  | 50  | 0.32 |
| SGM  | 60  | 0.37 | AM  | 60  | 0.31 |
| SGM  | 70  | -    | AM  | 70  | 0.29 |
| SGM  | 80  | 0.36 | AM  | 80  | 0.28 |

The $R_{\text{comp}}$ dependence on IOC volume is close to linear. The $R_{\text{comp}}$ curve trend in gypsum-magnetite compositions allows assuming that the material structure, i.e. type of base unit packing, size and shape of crystals, plays a leading role in strength stabilization. SEM imaging of the material microstructure was studied to confirm this assumption. The microstructure of SG-50 composition (Fig. 3 a) presented by thin, small, extended prismatic crystals differs from the microstructure of AM-50 composition (Fig. 3 b). CP-based compositions are exposed to fast hydration and hardening of a binder. At the same time, small extended prismatic crystals up to 8 $\mu$m long and 0.4-0.8 $\mu$m thick (Fig. 3 a) are formed, which, when overlapping, create the primary structure of a material due to crystallization. Larger magnetite particles are captured in voids between plaster crystals. Such structurization mechanism illustrates the curve trend with regard to material strength change in gypsum plaster (Fig. 2 a).

Up to 40 wt. % of IOC may be introduced into voids between CP crystals not damaging crystallization. A further increase in IOC volume will lead to damage of crystallization and a decrease in material strength. Plaster crystals cover magnetite particles. It is also confirmed by material color. Materials on the basis of G-4 are gray, while materials on the basis of anhydrite binder are intense black.

![Figure 2. Influence of IOC additives on strength: a) CP; b) An II](image)

![Figure 3. Microphotographs of composite materials: a – SGM–50; b – AM–50](image)
Anhydrite binding agents are hydrated differently. First of all, anhydrite even in the presence of hardening activators is hydrated more slowly than G-4. At first, anhydrite crystals are covered by a cracking pattern and split up into fine particles. Then, lamellar crystals begin to grow from this mass thus forming large crystals with a layered-package structure similar to IOC in size (Fig. 3 b). Parts of magnetite settle down between and on top of plaster crystals and deteriorate crystallization conditions. For this reason, the strength of composite materials on the basis of anhydrite binding agent steadily decreases with the increase in the IOC component (Fig. 3). Such materials are black. The identity index (Ki) depending on sizes of plaster microclusters [7] is higher for AM-30 (0.37) than that of SGM-30 (0.27). SGM-30 has a more finely-crystalline structure than AM-30. The X-ray pattern shows that the area and intensity of Fe$_3$O$_4$ reflexes of SGM-30 in case of interplanar spaces of 0.2974 and 0.2536 µm are slightly bigger than that of AM-30. This confirms changes of parameters of the magnetite crystalline lattice in plaster-magnetite compositions.

The main disadvantage of concrete used for the protection against ionizing radiation is its low thermal conductivity, which creates additional difficulties for heat transfer. In this regard, thermal performance of obtained materials was studied. Compositions of AM-50 and SG-50 were selected for further study. The material was molded in tiles of 15x15x2 cm in size. Effective thermal conductivity of gypsum plaster and anhydrate binder equals 0.2333 and 0.2399 W/m·K respectively. Thermal conductivity of SG-50 makes 0.2378 W/m·K and that of AM-50 makes 0.3052 W/m·K (Tab. 3).

**Table 3. Physical-mechanical properties of materials**

| No. | Initial composition | Features of obtained materials | R$_{comp}$; MPa | $\rho$; kg/m$^3$ | Thermal conductivity; W/m·K | $\mu_m$; cm$^2$/g |
|-----|---------------------|--------------------------------|-----------------|-----------------|---------------------------|-----------------|
| 1.  | CP*                 |                                | 17.6            | 1,200           | 0.2333                    | 0.0626          |
| 2.  | AnII **             |                                | 29.6            | 1,350           | 0.2399                    | 0.0626          |
| 3.  | AM–50**             |                                | 16.1            | 1,670           | 0.3052                    | 0.0714          |
| 4.  | SGM–50*             |                                | 9.4             | 1,500           | 0.2378                    | 0.0662          |

Introduction of IOC into gypsum plaster slightly increases thermal conductivity of plaster, which can be explained by its structure when magnetite particles are isolated from each other by plaster crystals. On the contrary, in case of anhydrite-based materials the magnetite is located between plaster crystals and partially on their surface, which increases thermal conductivity of a material. Over time there is clogging of plaster stone pores in gypsum-magnetite systems due to hydration and oxidation of Fe$_3$O$_4$ products consisting of hydroxide iron salts.

4. **Conclusions**

Calculation and experimental data demonstrate the possibility of using iron-ore concentrate of Lebedinsky GOK in the production of plaster concrete to ensure protection against the ionizing radiation.

It is found that physical-mechanical properties of composite materials depend on the type of plaster binding agent and its structures. CP-based materials have a finely-crystalline structure, which is presented by extended prismatic crystals forming a porous structure with a considerable number of pores. The material based on anhydrite binding agent consists of large crystals with a layered-package structure providing for more dense packing of crystals.

According to mass attenuation factor, the obtained material corresponds to protective properties of dense flints. Magnetite filler increases thermal conductivity of gypsum concrete on the basis of anhydrite binding agent by 25–30% and almost does not influence thermal conductivity of concrete on the basis of gypsum plaster. It is suggested to use gypsum-magnetite composite materials for gypsum partition blocks and plaster compounds when outfitting X-ray rooms.
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