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EFFECT OF 3d-METAL SALTS ON THE ACTIVITY OF ECOPHOSPHATE SLAG BINDING AGENTS

Abstract. It has been established that: 3d-metals of a number of manganese are effective at low doses (2 ... 4% by weight), over which the strength of slag stone decreases - the higher the dose, the more the strength decreases; cations $3d^{5-8}$ of which are capable of receiving electrons, effectively activate HFS, while the strength of slag (cement) stone with an addition of 2 ... 4% reaches 61 ... 97 MPa; moreover, manganese salts possess the highest strength, characterized by increased electron-acceptor properties (72 ... 97 MPa), the least - nickel salts (60 ... 72 MPa); with cations of copper ($3\ d^9$) and zinc ($3d^{10}$) extremely negatively affect the hardening of slag stone (21 ... 40 MPa); with cations whose hydrates have a spatial octahedral configuration, they effectively activate HFS; if cation hydrates have a distorted octahedral or tetrahedral configuration, then they adversely affect the hardening of slag (cement) stone.

Considering that the main elements of tobermorite gel and CSH (I) are Ca^{2+}, SiO_4^{4-} и OH^- (H_2O), ions, we can assume that: cations of 3d metal salts in the structure of calcium hydrosilicates replace Ca^{2+} ions according to the scheme $Me^{2+} \uparrow\downarrow Ca^{2+}$; in addition, impurity ions (Me^{2+}) in calcium hydrosilicates can be located outside structural bonds — in voids; ions SO_4^{2-} in hydrated phases can replace silicon-oxygen radicals according to the scheme $SO_4^{2-} \uparrow\downarrow SiO_4^{4-}$; the ions SO_4^{2-} replacing groups $Si_xO_y^{2-}$ in the structure of calcium hydrosilicates cannot create a continuous series in them; the ions Cl^- in the structure of calcium hydrosilicates can occupy three positions: to replace O^{2-}, OH^- and to be in voids.

Key words: Granulated phosphate slag, chlorides and sulfates of 3d transition metals, cations, electrons, acceptors, donors, strength, stone, calcium silicate hydrates.

Introduction. Works [1–4] show that the most effective way to neutralize granulated phosphate slag (hereinafter - GPS) from harmful gases (PH_3, H_2S, HF, etc.) and their sources are compounds of some transition 3d metals (Mn, Cu and Fe). Besides, we suggested that: the aforementioned oxides not only neutralize GPS, but can also activate it; the neutralizing activating ability of Mn, Cu, and Fe oxides is associated with the presence of electron-free orbitals on the 3d-sublevel of these elements.

Based on the above considerations, we can assume the following: the third-row elements from Cr to Zn, as well as their salts, can also have both neutralizing and activating GPS properties; the degree of their activity should be related to the number of electrons in 3d orbitals - the less electrons in them, the greater their activity as a neutralizer and activator.

It is known that the influence of the electron content in the 3d-sublevel of transition metals on cement activity was studied in [5–7]. Analyzing the results obtained, it can be stated that metal additives with electronic configuration d^{10} have an adverse effect on the strength of the hardening cement paste, and with configuration d^{2-8}, vice versa, they increase the strength of the cement stone compared to the strength of the control samples.

The adverse effect of d^{10} elements is due to the fact that their electrons, like donors, stop the movement of protons and neutralize active centers of the surface of cement particles, therefore its activity decreases or disappears. Since d^{2-8} elements, as acceptors, take electrons to empty orbitals from the surface of clinker minerals, they help increase the activation of the latter, and thereby increase the strength of the cement stone.

However, it should be noted that cement itself does not need to increase its activity by injecting such expensive additives - there are cheaper and more effective methods for this.

To neutralize harmful gases and their sources that are part of GPS, the relevant neutralizer is a vital measure, since it is associated with the social-environmental and environmental-economic direction of the southern regions of Kazakhstan, and more.

Research methodology. Chlorides and sulfates of a number of manganese were used as a GPS neutralizer, since they, as salts of strong acids, dissolve well in water, dissociating according to the scheme: $MeX \rightarrow Me^{2+}+X^{П}$, where Me – 3d-metal cation, $X^{П}$-SO^{2-} and Cl^{-}.

An ecophosphate slag binding agent was prepared with the addition of these salts using the wet method. GPS grinding with the addition of 2…8 % salts of 3d-metals was carried out in a vibratory mill to a specific surface of 500 m^2/kg without activating alkaline components in order to establish the degree of activating ability of these salts depending on the number of electrons on the 3d-sublevel. 2x2x2 cm samples were prepared from the test, which were then autoclaved at 180 °C according to the 2+8+2 hr mode and tested for compressive strength.

Results and discussion. It is established that: 3d-metals of a number of manganese are effective at low doses (2…4 % by weight), over which the slag stone strength decreases - the higher the dose, the more the strength decreases; cations $3d^{5-8}$ which are capable of receiving electrons, effectively activate GPS, while the strength of slag (cement) stone with an additive of 2…4 % reaches 61…97 MPa; moreover, manganese salts have the highest strength, characterized by increased electron-accepting properties (72…97 MPa), the least - nickel salts (60…72 MPa); with cations of copper ($3d^{9}$) and zinc ($3d^{10}$) have an extremely adverse effect on slag stone hardening (21…40 MPa); with cations whose hydrates have a space octahedral configuration, they effectively activate GPS; if cation hydrates have a distorted octahedral or tetrahedral configuration, then they adversely affect the hardening of slag (cement) stone.

Moreover, the increased activating ability of $3d^{5-8}$ cations (elements) compared to $3d^{10}$ cations (elements) is explained by the resulting action of the following three factors:

1. In the presence of cations (elements) of $3d^{5-8}$-metals, the basicity of the hardening system increases to a greater extent as a result of an increase in the content in the liquid phase of hydroxide groups (OH^{-}) accelerating its hydration and hardening;
2. Cations (elements) of $3d^{5-8}$-metals with electron-accepting properties attract electrons from the structure (bond) of portland cement and slag, as a result of which these bonds are lengthened (stretched); this contributes to an increase in the coordination number of silicon and the formation of intermediate unstable complexes, which favorably affects the hydration and hardening of hardening systems;
3. By creating $\equiv Si\text{-}O\text{-}Me^{+}$ bonds, cations (elements) of $3d^{5-8}$-metals interfere with the polymerization of silicon-oxygen anions to form calcium hydrosilicate nuclei, which increases the activity of the base portland cement and slag binders.

Thus: any additives that are electron acceptors activate portland cement and slag binders; if they are electron donors, then such additives can be inhibitors of hydration and hardening of hardening systems; initially, clinker minerals of portland cement (C_3S, β-C_2S, C_3A, C_4AF, etc.) and vitreous components of granulated slag have electrodonor properties, and the aqueous medium with which they are mixed during hydration and hardening must have electron-accepting properties in order to pull donor electrons from these minerals and glass; this is how hydration processes occur, followed by the transformation of the hardening system into stone.

The results obtained show that: with such a quantity, these additives in the hardening system do not remain in a free state and do not form independent compounds (both adversely affect the properties of cement stone, concrete and products), and will be included in the structure of tobermorite gel (C-S-H) and submicrocrystalline CSH (I); the endoeffect in the thermogram of the tobermorite gel that arose in the reference sample is recorded at 120 °C [8], and in the slag stone - at 140…260°C; the X-ray pattern of the reference sample contains CSH (I) diffraction maxima with interplanar spacings d = 3.07; 2.8 and 1.83 Å [8], and on the X-ray pattern of slag stone, reflections of this phase appear at Å: 3,00…3,12; 2,80…2,82 and 1,80…1,85.

Moreover: the endoeffect of the tobermorite gel on DTA shifts toward higher temperatures, which is due to the entry of ions of 3d-metal salts into its structure; in this case, impurity ions positively affect the state of tobermorite gel, as a result of which its effect appears at elevated temperatures; the exo-effect of CSH (I) on XRF shifts toward lower and higher temperatures compared to the exo-effect of the reference sample; this indicates a weakening of its structure in the first case and strengthening in the second case when ions of 3d-metal salts enter it; the entry of ions of 3d-metal salts into the CSH (I) structure shows both the expansion and the narrowing of interplanar spacings in the area of analytical line 3.03 Å in the X-ray pattern; moreover, impurity ions are more localized on the (220) CSH (I) plane than on the (400) and (040) planes.

Considering that the main elements of tobermorite gel and CSH (I) are Ca^{2+}, SiO_4^{4-} and OH$^-$ (H$_2$O) ions, we can assume that: cations of 3d-metal salts in the calcium silicate hydrate structure replace Ca^{2+} ions according to the Me^{2+}↑↓Ca^{2+} scheme; in addition, impurity ions (Me^{2+}) in calcium silicate hydrates can be located outside structural bonds — in voids; SO_4^{2-} ions in hydrated phases can replace silicon-oxygen radicals according to the SO_4^{2-}↑↓ SiO_4^{4-}scheme; while SO_4^{2-} ions replacing Si$_x$$O_y^{2-}$ groups in the calcium silicate hydrate structure cannot create a continuous series in them; this is due to the fact that SO_4^{2-} ions have an anisodesmic structure, and SiO_4^{2-}ions have a mesodesmic structure; in addition, in SO_4^{2-} ions, 2/3 of oxygen charge is associated with sulfur, while in SiO_4^{4-} ions only half of the oxygen charge is associated with silicon [9]; Cl$^-$ ions in the calcium silicate hydrate structure can occupy three positions: replace O^{2-}, OH$^-$ and be in voids.

Summary. 1.Sulphates and chlorides of 3d-metals of a number of manganese (metals themselves and their other compounds) used as neutralizing additives from harmful gases and their sources, that present in the composition of granulated phosphate slag, can simultaneously activate this slag.

1. The activating ability of 3d-metal compounds (including metals themselves) depends on the amount of electron-free 3d-orbitals. It is shown that cations (elements) of 3d$^{5-8}$-metals with electron-accepting properties activate mineral binders, while cations (elements) of 3d$^{9-10}$-metals, which have predominantly electron-donating properties, can be inhibitors of hydration of hardening systems.

2. With a small amount (2…4 %) neutralizing additives do not remain in a free state and do not form independent compounds, but enter into the structure of hydrated phases of hardening systems. At the same time, cations of neutralizing additives in the structure of calcium hydrosilicates can mainly replace Ca^{2+}, anions - silicon-oxygen radicals or hydroxide groups.

Confirmation. Scientific results were obtained within self-financing of TseLSIM LLP.

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3d-МЕТАЛЛ ТҰЗЫНЫҢ ЭКОФОСФОҚОЖ ТҰТҚЫР БЕЛСЕНДІЛІГІНЕ ӘСЕРІ

Аннотация. Зерттеу барысында мынадай үдерістер айқындалды: марғанец қатарындағы аз мөлшердегі (2...4% салмақ) 3d-металдары тиімді болғандықтан қож тасыныц қаттылығы төмендейді, доза көп болған сайын беріктігі әлсірей түседі; 3d$^{5-8}$ катиондары электрондарды қабылдауға қабілетті, ГФҚ тиімді белсендендіреді, бұл ретте 2...4%-ға қоса қож (цемент) тасыныц беріктігі 61...97 МПа жетеді; сонымен қатар, жоғары электронды-акцепторлық қасиеттер негізінде сипатталатын марғанец тұздары аса берік келеді (72... 97 МПа), ец азы – никель тұзы (60...72 МПа); мыс катиондары (3 d^9) және мырыш (3d^{10}) қож тасыныц қатаюына теріс әсер береді (21...40 МПа); кеңістік октаэдрикалық конфигурациясы бар катион ғидраттары ГФҚ тиімді белсендендіреді; егер катион ғидраттары бұрмаланған октаэдрикалық немесе тетраэдрикалық конфигурацияға ие болса, онда олар қож (цемент) тастарыныц қаттылығына теріс әсер етеді.

Зерттеу барысында мына мәселелерді атап көрсеткен жөн: аз мөлшерде берік жүйедегі бұл қоспалар бос күйінде қалмаумен қатар, дербес қосылыс та құрмайды (осы және басқалары цемент тасы, бетон мен бұйым қасиеттеріне теріс әсер етеді) және тоберморитті ғель (C-S-H) мен субмикрокристал СҢН (I) құрылымына кіреді; эталон үлгісінде пайда болған тоберморитті ғельдің термограммасында эндоэффект 120°С кезінде, ал қож таста 140...260°C болганда белгіленеді; эталонды үлгінің рентгенограммасында d=3,07 жазықаралық қашықтыгы СҢН (I) дифракциялық максимумнан тұрады: 2,8 және 1,83Å, ал қож тастарының рентгенограммасында Å: 3,00…3,12; 2,80…2,82 и 1,80…1,85 кезінде осы фаза көріністері пайда болады.

Тоберморитті гель мен СҢН (I) негізгі элементтері Ca^{2+}, SiO_4^{4-} және OH^- (H_2O) ионы екенін ескере отырып, кальций гидросиликат құрылымындағы 3d-металл тұзыныщ катионын Ca2+ иондарына $Me^{2+}\uparrow\downarrow Ca^{2+}$ схемасы бойынша алмастыруга болады; сонымен қатар, кальций гидростиликатындағы қоспалы иондар (Me^{2+}) құрылымдық байланыстан тыс – бос жерде мүмкін; гидратты фаздагы SO_4^{2-} иондар $SO_4^{2-}\uparrow\downarrow SiO_4^{4-}$ сызбасы бойынша кремний тотықты радикалдарды алмастыра алады; сонымен қатар SO_4^{2-} иондар кальций гидросиликат құрылымындағы $Si_xO_y^{2-}$ топқа орналасқанда үздіксіз қатар түзе алмайды; кальций гидросиликат құрылымындагы Cl^- иондар O2- орын алмастыру, OH^- және бос қалу сынды үш позиция иеленуі мүмкін.

Түйін сөздер: Түйіршіктелген фосфор қожы, 3d-өтпелі металл хлориді мен сульфаты, катиондар, электрондар, акцепторлар, донорлар, беріктік, тас, кальций гидросиликаттары.

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ВЛИЯНИЕ СОЛЕЙ 3d-МЕТАЛЛОВ НА АКТИВНОСТЬ ЭКОФОСФОШЛАКОВЫХ ВЯЖУЩИХ

Аннотация. Установлено, что 3d-металлы ряда марганца эффективны при малых дозах (2…4 % по массе), сверх которых прочность шлакового камня снижается: чем больше доза, тем больше снижается прочность; катионы, $3d^{5-8}$ которых способны принимать электроны, эффективно активизируют ГФШ, при этом прочность шлакового (цементного) камня с добавкой 2…4 % достигает 61…97 МПа; причем наибольшей прочностью обладают марганцевые соли, характеризующиеся повышенными электронно-акцепторными свойствами (72…97 МПа), наименьшей – никелевые соли (60…72 МПа); с катионами меди ($3\ d^9$) и цинка ($3d^{10}$) чрезвычайно отрицательно влияют на твердение шлакового камня (21…40 МПа); с катионами, гидраты которых имеют пространственную октаэдрическую конфигурацию, эффективно активизируют ГФШ; если же гидраты катионов обладают искаженной октаэдрической или тетраэдрической конфигурацией, то они отрицательно влияют на твердение шлакового (цементного) камня.

Показано, что при малом количестве эти добавки в твердеющей системе не остаются в свободном состоянии и не образуют самостоятельных соединений (те и другие негативно действуют на свойства цементного камня, бетона и изделий), будут входить в структуру тоберморитового геля (C-S-H) и субмикрокристаллического CSH (I); эндоэффект в термограмме тоберморитового геля, возникшего в эталонном образце, фиксируется при 120°С, а в шлаковом камне – при 140…260°С; на рентгенограмме эталонного образца присутствуют дифракционные максимумы CSH (I) с межплоскостными расстояниями d=3,07; 2,8 и 1,83Å, а на рентгенограмме шлакового камня появляются отражения этой фазы при Å: 3,00…3,12; 2,80…2,82 и 1,80…1,85.

Учитывая, что основными элементами тоберморитового геля и CSH (I) являются ионы Ca^{2+}, SiO_4^{4-} и OH^- (H_2O), можно допустить, что катионы солей 3d-металлов в структуре гидросиликатов кальция замещают ионы Ca^{2+} по схеме $Me^{2+}\uparrow\downarrow Ca^{2+}$; кроме того, примесные ионы (Me^{2+}) в гидросиликатах кальция могут находиться вне структурных связей – в пустотах; ионы SO_4^{2-} в гидратных фазах могут замещать кремнекислородные радикалы по схеме $SO_4^{2-}\uparrow\downarrow SiO_4^{4-}$; при этом ионы SO_4^{2-} , замещая группы $Si_xO_y^{2-}$ в структуре гидросиликатов кальция, не могут создавать в них непрерывный ряд; ионы Cl^- в структуре гидросиликатов кальция могут занимать три позиции: замещать O^{2-}, OH^- и находиться в пустотах.

Ключевые слова: гранулированный фосфорный шлак, хлориды и сульфаты 3d-переходных металлов, катионы, электроны, акцепторы, доноры, прочность, камень, гидросиликаты кальция.

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