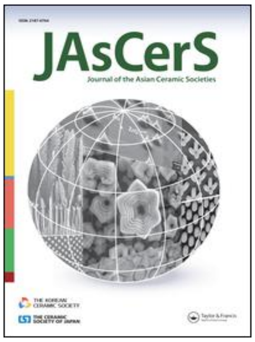

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FULL LENGTH ARTICLE

Influence of Cr^{3+}, Co^{2+} and Cu^{2+} on the formation of calcium silicates hydrates under hydrothermal conditions at 200 °C

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ABSTRACT
This work aims to investigate the influence of Cr^{3+}, Co^{2+} and Cu^{2+} on the formation of calcium silicates hydrates in $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}H_2O$ system under hydrothermal conditions. The dry primary mixture with the molar ratio $CaO/(SiO_2+ Al_2O_3) = 1.5$ and $Al_2O_3/(Al_2O_3+ SiO_2) = 0.05$ was mixed with heavy metal nitrate solutions (metal ions concentration – 10 g/l) to reach the water/solid ratio of the suspension equal to 10.0. The hydrothermal synthesis was carried out in unstirred suspensions, under saturated steam pressure at 200°C temperature for 0–72 hours. It was determined that nature of metal ions have influence on both mineral composition and thermal stability of synthesis products. It was obtained that by increasing synthesis temperature up to 200°C, all Cr^{3+} and Co^{2+} ions were intercalated into the structure of synthesis products. Meanwhile Cu^{2+} ions participate in chemical reactions and as a result copper oxide were formed. The products of synthesis were characterized by STA, DSC, XRD and AAS analyses.

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Calcium silicate hydrates; heavy metal ions; hydrothermal synthesis; metal oxides; calcium chromate

1. Introduction

The enormous increment of greenhouse gas (GHG) emission (up to 50% by 2050) and waste generation leads to environmental concerns: air, water, and soil pollution, global warming, health issues and other perilous impacts [1,2]. There are many ways to reduce GHG emission (capture and store, to use alternative energy sources, to use new production technologies), however, to significantly reduce GHG impact on the environment the conversion technologies of it (especially CO_2 gas) should be developed and used worldwide [3]. The conversion technologies require a large amount of very expensive catalysts because precious metals (Pt, Pd, Au) are used as active components [4–6]. Besides, the application of traditional catalysts is limited by their thermal resistance, little reserves, due to difficulties in recovery, secondary pollution, etc.

For these reasons, there is growing interest in developing unconventional, environmentally friendly catalysts, which are cheaper and more resistant for catalyst poisons [7,8]. According to literature, calcium silicates, calcium silicates hydrates (CSH) and calcium aluminum silicates hydrates (CASH) with intercalated metal ions have the aforementioned properties and can be applied in many catalyst reactions. According to Olszowka et al. [9] even pure (without metals) magnesium and/or calcium containing minerals, can be used as environmentally friendly catalysts for manufacturing ε-caprolactone. Furthermore, Shimizu et al. [10] found that $Ni/CaSiO_3$ (nickel nanoparticles loaded onto calcium silicate) has a good catalytic activity for the synthesis of primary amines from alcohols and NH_3 under relatively mild conditions. Meanwhile, Segawa et al. [11] found that copper and calcium silicate could be used as an eco-friendly substitute for conventional copper chromium catalysts. Further, Shao et al. [12] showed that CSH substituted with heavy metal ions can be converted into efficient photocatalyst for methylene blue degradation (degradation efficiency about 90% by using a UV light for 150 min). Also, these compounds can be applied in many other catalytic reactions: dry reforming [13]; synthesis of bisphenol F [14], reforming of benzene [15], etc. When conventional catalysts lose their properties, they are stored in a landfill site, or are recycled by using expensive technologies. Meanwhile, calcium silicates hydrates with intercalated metal ions can be used for the production of ordinary Portland cement, during which the metal ions will be bound to stable compounds [16,17]. This method is usually used for the utilization of CSH with intercalated radioactive isotopes [18,19].

Although calcium silicate hydrates have good properties and can be applied in the catalysis process, still there is a great challenge to synthesize them and to intercalate metal ions without losing necessary properties (thermal stability, resistance, surface area). According to literature, the formation and application of the mentioned compounds depend on various parameters: used raw materials and additives, CaO/SiO_2 molar ratio of primary mixture,

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the duration and temperature of synthesis [20,21]. Most of calcium silicate hydrates can be synthesized in mixtures of calcium [22] and silica [23,24] containing compounds, under hydrothermal conditions in a 100–350°C temperature range [25].

According to the literature, adsorption is a commonly used method for the intercalation of metal ions into the structure of CSH. The adsorption process for Ti^{4+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Na^{+}, K^{+}, Cr^{3+}, Cu^{2+} and others ions by lower basicity CSH ($CaO/SiO_2 < 1.2$) are examined in detail. Meanwhile, the literature concerning the adsorption of metal ions by dibasic calcium silicate hydrates ($CaO/SiO_2 > 1.2$) is scarce. Niuniavaite et al. [26] showed that Cr^{3+}, Cu^{2+}, and Co^{2+} ions could be adsorbed by synthetic CSH, which CaO/SiO_2 molar ratio was equal to 1.5. The adsorption capacity of metal ions by CSH depends on the nature of adsorbent and adsorbate, temperature, pH value of the liquid medium, etc. In spite of the fact that adsorption by CSH is a low cost and simple operation, but also it is facing some disadvantages. Usually, the synthetic CSH is in a powder state, those it is quite hard to separate them from the liquid medium after adsorption. These compounds could be granulated, however, they lose surface area. Also, adsorption by CSH is facing many other issues such as weak selectivity, secondary pollution, the phenomena of swelling, disintegration, and agglomeration of adsorbent, stability in an acid liquid medium, etc [27–29].

Another way to intercalate metal ions into the structure of CSH is to use metal ions additives during synthesis. This method is tested or is using for the intercalation of many metals ions (Al^{3+}, Na^{+}, K^{+}, Cd^{2+}, Cu^{2+}, Zn^{2+} etc.) [30–32]. However, the scientific literature concerning the data of transition metals' influence on the properties and formation of calcium silicates hydrates under hydrothermal conditions are scare. Therefore, the aim of this work is to investigate the influence of Cr^{3+}, Co^{2+}, and Cu^{2+} on the formation of calcium silicate hydrates in $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}H_2O$ system under hydrothermal conditions.

2. Materials and methods

In this work, the following reagents were used:

(1) CaO was obtained by calcining $Ca(OH)_2$ ("Honeywell", Germany) at 550°C temperature for 1 hour and afterward was ground for 30 s in a vibrating cup mill "Pulversitte 9" (speed: 600 rpm). The surface area obtained by using "CILAS ID 1090" granulometer – 1889 m^2/kg, the quantity of free CaO – 93 wt. %.

(2) Amorphous $SiO_2 \cdot nH_2O$ ("Reaktiv", Russia) was ground for 3 min in a vibrating cup mill (speed: 900 rpm). The surface area – 2073 m^2/kg, the loss of ignition – 6.39%.

(3) $\gamma\text{-}Al_2O_3$ was obtained by calcining $Al_2O_3 \cdot nH_2O$ ("Honeywell", Germany) at 475°C temperature for 4 hours and afterward was ground for 30 s in a vibrating cup mill (speed: 600 rpm). The surface area – 650 m^2/kg.

(4) Cr^{3+}, Co^{2+} and Cu^{2+} solutions (10 g/l) were obtained by dissolving $Cr(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ or $Cu(NO_3)_2{\cdot}3H_2O$ ("Eurochemicals", EU) in distilled water.

The dry primary mixture with the molar ratios $CaO/(SiO_2+ Al_2O_3) = 1.5$ and $Al_2O_3/(Al_2O_3+ SiO_2) = 0.05$ was homogenized in a plastic container with 3 milling bodies of porcelain (to ensure the quality of homogenization) in the apparatus "TURBULA TYPE 2 F" for 45 min (speed: 49 rpm).

Later on, the obtained mixture was mixed with nitrate solutions to reach the water/solid ratio of the suspension equal to 10.0. The hydrothermal synthesis was carried out in unstirred suspensions, in 25 ml volume PTFE cells which were placed in a stainless steel autoclave (Parr Instruments, Germany), under saturated steam pressure at 200°C temperature for 4, 8, 16, 24, 48 and 72 hours by applying extra argon gas (1 MPa). The synthesis temperature was reached within 2 h. After the synthesis, the suspensions were filtered off, products rinsed with ethanol to prevent carbonization of materials, dried in air conditioning chamber at 50 °C ± 5 temperatures for 24 h, and sieved through a sieve with an 80 μm mesh.

The mineral composition of synthesis products was determined by using powder X-ray diffraction analysis (XRD; with a D8 Advance (AXS Bruker, Germany)), while thermal stability and phase transformation by simultaneous thermal analysis (STA, with Linseis PT1000 instrument (Linseis, Germany)) and differential scanning calorimetry (DSC, with Netzcsh Polyma DSC 214 (Netzcsh, Germany)) [33]. The liquid medium was investigated by using pH meter (with a Hanna instrument Hi 9321 pH meter (Hanna Instruments, USA)) and atomic absorption spectroscopy (AAS, with a Perkin-Elmer Analyst 4000 spectrometer (Perkin Elmer, USA)).

3. Results and discussion

3.1. CSH formation in $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}H_2O$ system

It was determined that the formation sequence of calcium silicates hydrates in the mixtures with the molar ratio of $CaO/(SiO_2+ Al_2O_3) = 1.5$ and $Al_2O_3/(SiO_2+ Al_2O_3) = 0.05$ under hydrothermal conditions at 200°C are similar to that reported in the literature [25,34–37]. For this reason, in this work, only a short discussion of compounds in $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}H_2O$ system formation is presented. It was obtained, that by increasing synthesis temperature to 200°C,

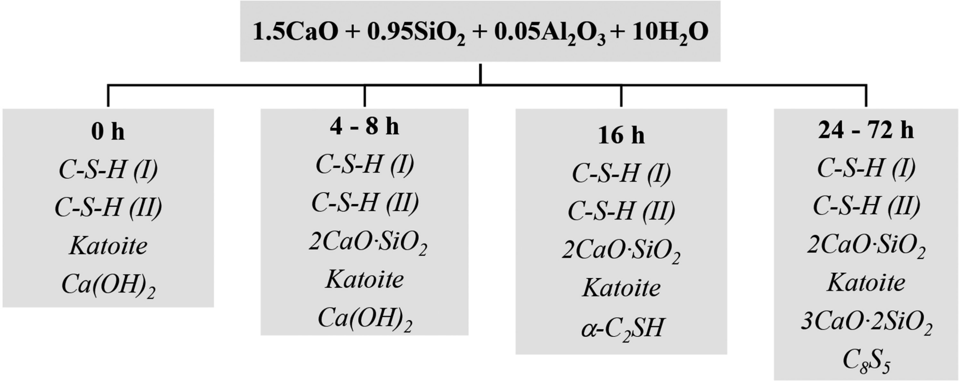

Figure 1. The sequence of CSH formation in $CaO-SiO_2-Al_2O_3-H_2O$ system under hydrothermal conditions at 200°C.

the formation of semi-crystalline calcium silicate hydrates (C-S-H(I) and C-S-H(II)) and calcium aluminate hydrate (katoite) proceeded (Figure 1). Also under these synthesis conditions, a fair amount (~17.3%) of unreacted portlandite are presented in the products.

By prolonging the duration of isothermal curing to 4–8 h, dibasic calcium silicate ($2CaO·SiO_2$) was formed in the products (Figure 1). The formation of anhydrous silicate under hydrothermal conditions are in good agreement with the literature data [38,39].

By continuing the synthesis (16 h), portlandite was fully reacted and a new synthesis product – $α-C_2SH$ ($2CaO·SiO_2 · 2H_2O$) was formed. According to TGA data, it was calculated that 30% of the latter compound is presented in the sample. Furthermore, after 24–72 h of hydrothermal treatment, the mixture of semicrystalline CSH, calcium silicates (kilchoanite, C_8S_5 and dicalcium silicate) and katoite were formed. The more details about compounds crystallization in $CaO-SiO_2-Al_2O_3-H_2O$ system under hydrothermal conditions are available in ref. [34,35].

3.2. The influence of Cr^{3+} ions on the calcium silicate hydrates formation

It was determined that in the system with chromium ions (c = 10 g/l), by increasing synthesis temperature up to 200°C, the interaction between primary compounds proceeded intensively, because portlandite was fully reacted and semi-crystalline type calcium silicate hydrates C-S-H (I) and/or C-S-H (II) (PDF No. 00–034-0002 and/or PDF No. 00–033-0306) were dominant in the products (Figure 2, curve 1). The identification of compounds containing aluminum ions is complicated, because part of these ions intercalated to the structure of CSH [40,41], while another part reacted with calcium and silicon ions and form low quantity or low crystallinity calcium aluminate hydrate (CAH) or calcium aluminum silicate hydrate (CASH) [40,42–44]. It is worth mentioning, that the low intensity peak at 0.167 nm could be related to CAH formation; however, in the XRD pattern other peaks characteristic to these compounds were not observed (Figure 2).

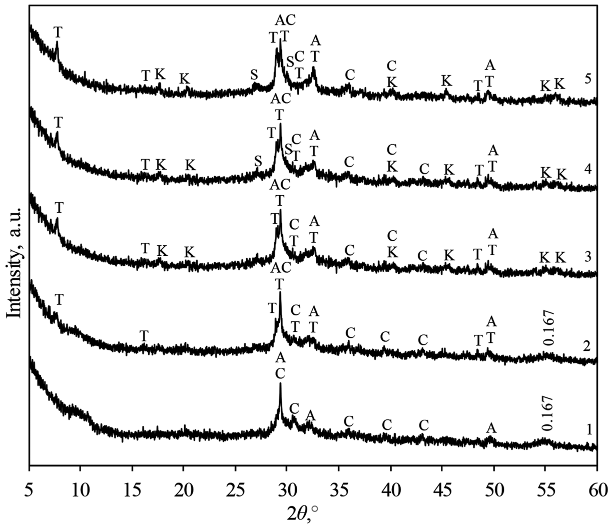

Figure 2. XRD patterns of synthesis products obtained in the mixtures with Cr^{3+} additive, when the duration of synthesis was equal to, h: 1–0; 2–4; 3–8; 4–16; 5–72. Indexes: A – C-S-H (I) and/or C-S-H (II); C – calcite; K – katoite; S – scawtite; T – tobermorite.

Also under all synthesis conditions, the carbonation proceeded, when the products were dried in an air conditioned chamber (80°C, 24 h) [34,35] because the diffraction peaks characteristic to calcite (PDF No. 04–012-0489) were observed (Figure 2).

It was determined that all Cr^{3+} ions were intercalated into the structure of synthesis products, because no other compounds, than mentioned previously, were detected in XRD patterns (Figure 2). This fact was also confirmed by the results of Atomic Absorption Spectroscopy because after synthesis the concentration of investigated heavy metal ions in the liquid medium did not exceed even 0.01%. The same tendency was observed under all experimental conditions.

The previous results were confirmed by a Simultaneous Thermal Analysis: a broad endothermic effect at 84°C temperature can be assigned to the removal

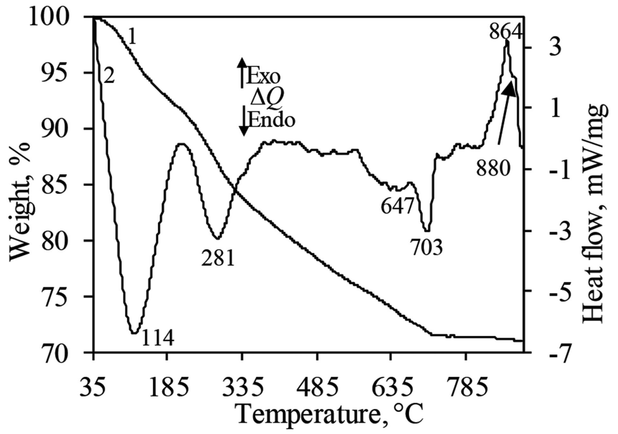

Figure 3. STA curves (1 – TG; 2 – DSC) of synthesis products obtained in the mixtures with Cr^{3+} additive, when the duration of synthesis was 0 h.

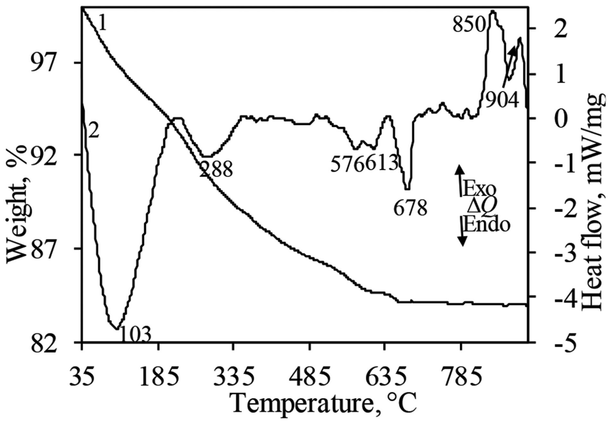

Figure 4. STA curves (1 – TG; 2 – DSC) of synthesis products obtained in the mixtures with Cr^{3+} additive, when the duration of synthesis was 4 h.

of chemically bound water in semicrystalline or amorphous CSH [45–47] (Figure 3). Since the results of XRD do not showed the formation of crystalline compounds in $CaO-SiO_2-Al_2O_3-Cr(NO_3)_3-H_2O$ system (except calcium carbonate), the effect at 272°C temperature can be attributed to the decomposition of low crystallinity compounds (CAH, CASH or compounds containing nitrate anion) [46,48] as well as to Cr^{3+} oxidation to Cr^{6+} (chromates formation) [49]. Meanwhile, the endothermic effects in a 550–700°C temperature range can be assigned to the formation of chromates [49] and decomposition of calcium carbonate. Furthermore, exothermic effect with a shoulder reflecting recrystallization process of C-S-H (I) (864°C) and C-S-H (II) (880°C) to wollastonite were observed above 800°C (Figure 4). It is worth mentioning that, due to the incorporation of Al^{3+} and Cr^{3+} ions into the structure of C-S-H (I) and C-S-H (II), the latter effects were shifted to a higher temperature in comparison with the results, which were obtained by others authors [50].

After 4 hours of isothermal curing, the traces of a new calcium silicate hydrate – 1.1 nm tobermorite ($Ca_5Si_6O_{17}(OH)\cdot 5H_2O$); PDF No. 00–019-0052) – were identified (Figure 2, curve 2). It is worth mentioning that the molar ratio of the mentioned compound is 1.8 times lower ($CaO/SiO_2 = 0.83$) in comparison with the molar ratio of the primary mixture ($CaO/(SiO_2+ Al_2O_3) = 1.5$). These results differ from the data presented in the literature [40,41], in which, the formation of calcium silicates hydrates in CaO and SiO_2 mixtures ($CaO/SiO_2 = 1.5–2$) was thoroughly examined. In these works [34,50], hillebrandite ($Ca_2SiO_3(OH)_2$), α-C_2SH ($Ca_2SiO_4\cdot H_2O$), kilchoanite ($Ca_3Si_2O_7$) and other C-S-H phases where synthesized, however, 1.1 nm tobermorite was not obtained. Also, according to the literature, the mentioned compound only forms in the mixtures, which CaO/SiO_2 varies in a 0.75–1 range and is not stable at hydrothermal synthesis temperature higher than 150°C [51–53]. Presumably, chromium and aluminum ions not only incorporated to the structure of synthesis products but also reacted with calcium ions and as a result, the molar ratio of CaO/SiO_2 in the mixture decreased. Another reason could be that the mentioned ions change the solubility rate of primary compounds (accelerate SiO_2 and retire CaO) and stabilize 1.1 nm tobermorite.

The sample with Cr^{3+} ions obtained after 4 h showed a similar DSC curve (Figure 4) as the sample, which was obtained after 0 h of isothermal curing (Figure 3). The main difference is the number of thermal conversions observed in the 800–950°C temperature range: after 4 h of synthesis two significant exothermic effects were noticed (Figure 4). The first exothermic effect with the shoulder can be assigned to the C-S-H (I) recrystallization to wollastonite, while the second – to C-S-H (II) with incorporated aluminum ions. Also, the loss on ignition decreased more than 10%, i.e. from 25.47% in the sample obtained after 0 h of synthesis to 16.00% in the sample obtained after 4 h of synthesis (Figure 3, curve 1 and Figure 4, curve 1). The changes in mass could be related to the increases of synthesis products crystallinity (mainly CSH).

By extending the synthesis duration (8 h), the traces of compound containing aluminum – katoite ($Ca_3Al_{2.85}O_{2.55}(OH)_{9.45}$; PDF No. 04–017-1504) were formed (Figure 2, curve 3). According to the scientific literature [40], the formation of calcium aluminates hydrates is possible if the quantity of unreacted SiO_2 in the mixture is lower than 40%, otherwise, calcium aluminum silicate hydrates will form.

After 16–72 h of isothermal curing, there were no significant changes in the mineralogical composition of synthesis product, only the traces of scawtite ($Ca_7Si_6(CO_3)O_{18}\cdot 2H_2O$; PDF No. 31–261) was detected in XRD patterns (Figure 2, curves 4 and 5). It is worth mentioning, that scawtite is a carbonized calcium silicate hydrate [54], which probably occurred due to the interaction between CSH and dissolved CO_2, which was present in

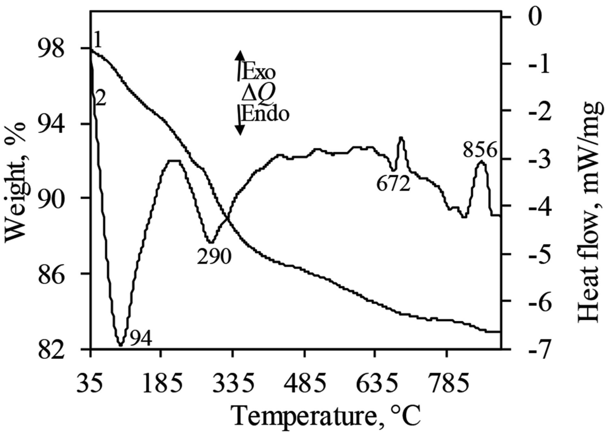

Figure 5. STA curves (1 – TG; 2 – DSC) of synthesis products obtained in the mixtures with Cr^{3+} additive, when the duration of hydrothermal treatment at 200°C was equal to 24 h.

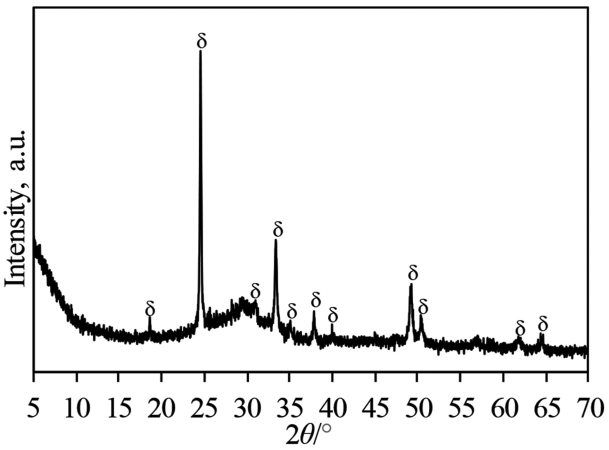

Figure 6. XRD pattern of synthesis products with Cr^{3+} ions calcined at 700°C temperature for 1 h. Indexes: δ – calcium chromate.

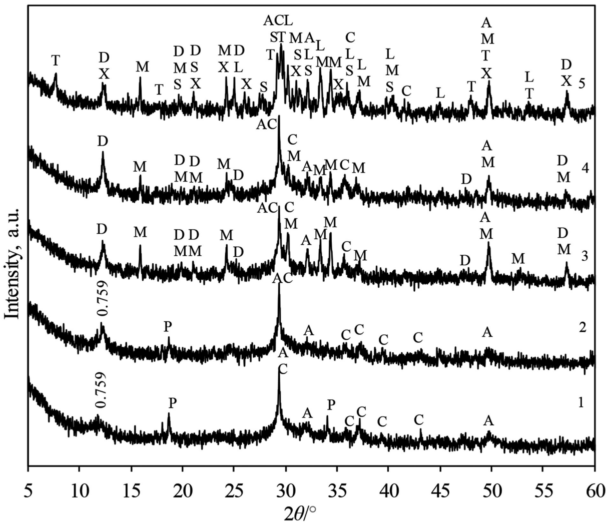

Figure 7. XRD patterns of synthesis products obtained in the mixtures with Co^{2+} additives, when the duration of synthesis was equal to, h: 1–0; 2–4; 3–8; 4–24; 5–72. Indexes: A – C-S-H (I) and/or C-S-H (II); C – calcite; D – kaolinite and/or dickite; L – kilchoanite; M – monticellite; P – portlandite; S – scawtite; T – tobermorite; X–xonotlite.

the distilled water. These results are in good agreement with the data obtained by Števula et al. [55], who reported that scawtite can form in $CaO\text{-}SiO\text{-}H_2O$ mixtures, which CaO/SiO_2 molar ratio is equal to 1.2, 1.6 and 2.0, under hydrothermal conditions at 200°C. Also, the similar results were obtained by Pytel [56], who performed synthesis in a $CaO\text{-}SiO_2\text{-}CO_2\text{-}H_2O$ system.

The STA curves of synthesis products obtained after 24 h are presented in Figure 5. The main difference, in comparison to the STA data discussed above (Figures 3 and 4), is the number of thermal conversions observed in a 500–700°C temperature range: after 24 h of synthesis only one endothermic effect was noticed (Figure 5).

In order to confirm the nature of the thermal conversion in the 550–700°C temperature range, the sample was calcined in a high temperature furnace at 700°C temperature for 1 h and, later on, the XRD analysis was performed (Figure 6). It was determined that, after calcination, only one crystalline compound – calcium chromate ($CaCrO_4$; PDF No. 01–087-1647) was formed in the products. The broad basal reflection in the 20–40° 2*θ* range corresponds to the partially dehydrated calcium silicate hydrates [53].

3.3. The influence of Co^{2+} ions on the calcium silicate hydrates formation

In the next stage of this work, the influence of Co^{2+} ions, which are widely used in the catalyst process [57–59] on the formation of calcium silicates hydrates was investigated. It was determined, that by increasing hydrothermal treatment temperature to 200°C in $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Co(NO_3)_2\text{-}H_2O$ system C-S-H (I), C-S-H (II) and calcite (due to carbonization in air conditioning chamber) were formed (Figure 7, curve 1). Under these synthesis conditions, the intensive diffraction peaks characteristic to unreacted portlandite ($Ca(OH)_2$; PDF No. 00–01-1079) were observed in the XRD pattern (Figure 7, curve 1). It is worth mentioning that in the mixtures with Cr^{3+} ions this compound fully reacted at the beginning of synthesis (Figure 2, curve 1).

Also in the XRD pattern quite intensive diffraction peak at 0.759 nm, which was not assigned, was noticed (Figure 7, curve 1, 2). This peak could be related to the formation of aluminum containing compounds, unfortunately, the identification based on one *d*-spacing is inaccurate.

It was determined that the thermal behavior of synthesis products is quite complex (Figure 8). The first endothermic effect at ~85°C temperature corresponds to the removal of chemically bound water in semicrystalline or amorphous CSH. Then, the existence of unreacted portlandite was proved by an endothermal peak in a 380–450°C temperature range (Figure 8)

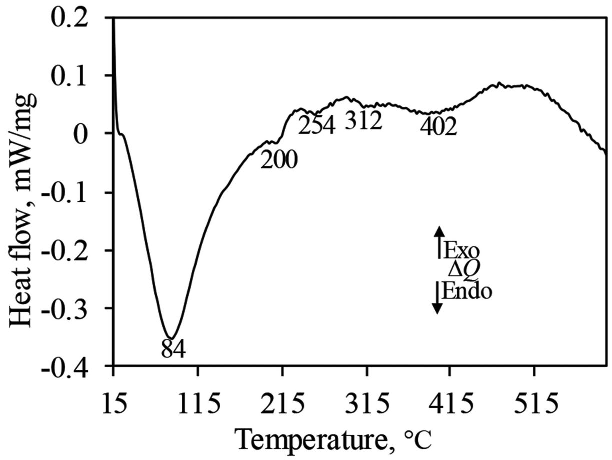

Figure 8. DSC curve of synthesis products obtained in the mixtures with Co^{2+} additive, when the duration of synthesis was 0 h.

[46,60]. Further the small thermal conversions in 200–350°C temperature range can be attributed to the decomposition of low crystallinity or amorphous compounds, which were not detected in the XRD pattern [46,47] (Figure 8).

The mineralogical composition of synthesis products obtained after 4 h of isothermal curing are similar to that obtained after 0 h (increment of synthesis temperature) (Figure 7, curves 1 and 2). The main difference is the changes of diffraction peaks intensity. The AAS analysis of liquid medium obtained after 0–4 h of synthesis showed, that concertation of Co^{2+} ions did not exceed even 0.01%. Thus, it can be stated, that all Co^{2+} ions were intercalated into the structure of CSH because compounds containing mentioned ions were no detected in the XRD pattern (Figure 7, curve 1, 2).

The significant changes were obtained after 8 h of synthesis: firstly, portlandite was fully reacted (Figure 7, curve 3). Secondly, compounds containing aluminum, kaolinite ($Al_2Si_2O_5(OH)_4$; PDF No. 00–058-2005) and/or dickite ($Al_2\ Si_2O_5(OH)_4$; PDF No. 00–058-2002) were formed (Figure 7, curve 3). The possibility of kaolinite formation under hydrothermal conditions in the 150–200°C temperature range was proved by Huertas et al. [61]. It is worth mentioning, that diffraction peak with *d*-spacing – 0.759 nm identified after 0–4 h of isothermal curing (Figure 7, curves 1 and 2), could be related to the beginning of kaolinite and/or dickite crystallization. Unfortunately, there was no other peak characteristic to mentioned compounds.

Thirdly, it was found that the formation of crystalline calcium silicates hydrates is a complex process, because in the system with Co^{2+} additive, due to a strong interaction between cobalt ions and calcium silicates (probably olivine), cobalt calcium silicate – monticellite ($Ca_{1.255}Co_{0.745}SiO_4$; PDF 04–014-9775) was formed (Figure 7, curve 3). The formation of this compound is possible by a reaction:

$$0.745Co^{2+} + Ca_2SiO_4 \rightarrow Ca_{1.255}Co_{0.745}SiO_4 + 0.745Ca^{2+} \quad (1)$$

It is worth mentioning that naturally monticellite forms during ion exchange reactions and its chemical composition is $Ca_{(x\text{-}y\text{-}z)}Mg_yFe_zSiO_4$ ($x < 2$) [61].

As expected, the analysis of liquid medium showed, that the concertation of Co^{2+} ions was less than 0.01%. Thus, under these synthesis conditions, the Co^{2+} ions participated in chemical reactions (Equation 1).

The formed compounds remained stable in the $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Co(NO_3)_2\text{-}H_2O$ system when the synthesis duration was extended from 8 to 16–24 h (Figure 7, curve 4).

The previously discussed results coincide with the data of STA of synthesis products obtained after 24 h of isothermal curing. The sample with Co^{2+} ions showed 5 endothermic and 1 exothermic effects (Figure 9). The first two endothermic effects (107°C and 217°C) correspond to the loss of adsorption water as well as dehydration of CSH. Meanwhile, the thermal conversions at 474°C and 602°C temperatures can be assigned to the dehydration of dickite and kaolinite [62,63]. According to the literature, the decomposition of the mentioned compounds proceeds gradually in a 400–700°C temperature range, thus these effects cannot be assigned to a specific compound [62,63]. The last endothermic effect (698°C) corresponds to the decomposition of calcite and/or to compaction of metastable dickite and kaolinite decomposition products [46,62]. Finally, at 837°C temperature, semicrystalline calcium silicate hydrates recrystallized to wollastonite (Figure 9).

Meanwhile, when the duration of isothermal synthesis was prolonged to 48–72 h, together with previously recognized compounds (kaolinite and/or dickite, monticellite, C-S-H (I) and/or C-S-H (II)) new crystalline calcium silicates hydrates – kilchoanite

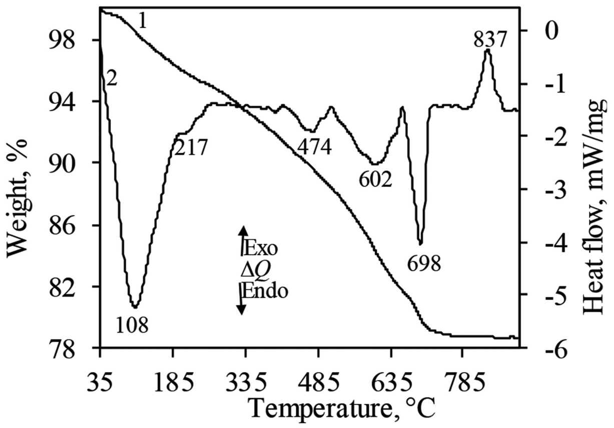

Figure 9. STA curves (1 – TG; 2 – DSC) of synthesis products obtained in the mixtures with Co^{2+} additive, when the duration of synthesis was 24 h.

(PDF 00–029-0370), scawtite, 1.11 nm tobermorite and xonotlite ($Ca_6Si_6O_{17}(OH)_2$ PDF No. 04–016-1649) were identified (Figure 7, curve 5). It is worth mentioning that the molar ratio of tobermorite ($Ca/SiO_2 = 0.83$) and xonotlite ($Ca/SiO_2 = 1.0$) is lower than the initial mixture ($Ca/SiO_2 = 1.5$), meanwhile the molar ratio of kilchoanite is equal to 1.5. According to the literature [56], pure kilchoanite (> 95%) can be synthesized in $1.5CaO\text{-}SiO_2\text{-}H_2O$ system under hydrothermal conditions (200°C; 48 hours). While other sources [41,64] state that this compound can also form from β-C_2S, during the hydrothermal synthesis of α-C_2SH, or during an oil well cement hydration at 200°C. It can be stated, that Co^{2+} ions strongly affect the formation of crystalline CSH, because in pure system kilchoanite is dominant compound after 24–72 h of isothermal curing (Figure 1), meanwhile, in the system with Co^{2+} ions, the mixture of CSH and CASH were obtained (Figure 7, curve 5).

3.4. The influence of Cu^{2+} ions on the calcium silicate hydrates formation

In the last part of this work, the influence of Cu^{2+} ions on the formation of compounds in the $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Cu(NO_3)_2\text{-}H_2O$ system under hydrothermal conditions were examined. It was determined, that the interaction between primary compounds differs from previously discussed cases (Cr^{3+} and Co^{2+}), because at the beginning of synthesis (0 h) together with C-S-H (I), C-S-H (II) and calcite, intensive diffraction peaks of copper oxide (CuO; PDF No. 04–007-1375) were identified (Figure 10, curve 1). Also under these synthesis conditions, the traces of copper hydroxide ($Cu(OH)_2$; PDF No. 00–035-0505) were observed.

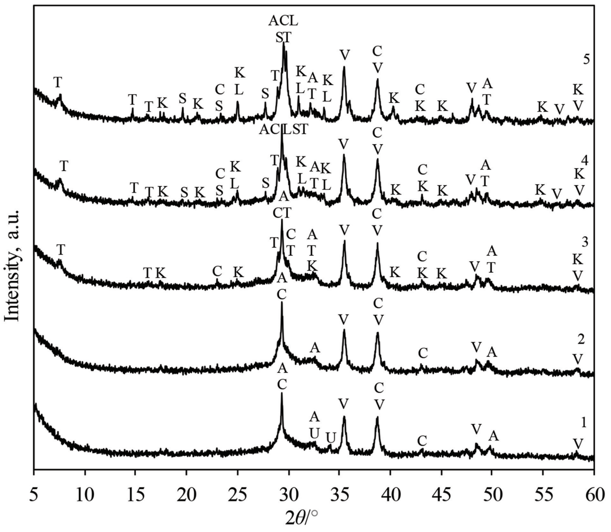

Figure 10. XRD patterns of synthesis products obtained in the mixtures with Cu^{2+} additives, when the duration of synthesis was equal to, h: 1–0; 2–4; 3–8; 4–16; 5–72. Indexes: A – C-S-H (I) and/or C-S-H (II); C – calcite; K – katoite; L – kilchoanite; S – scawtite; T – tobermorite; U – copper hydroxide; V – copper oxide.

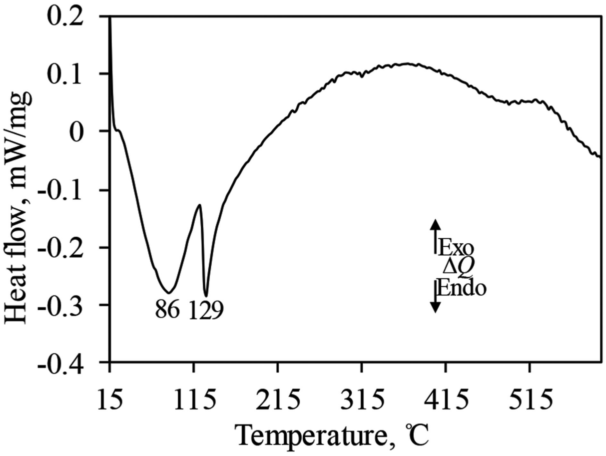

Figure 11. DSC curve of synthesis products obtained in the mixtures with Cu^{2+} additive, when the duration of hydrothermal treatment at 200°C was equal 0 h.

The existence of copper hydroxide was proved by DSC analysis: the first endothermic effect belongs to the removal of chemically bound water, while the second one (129°C) belongs to the decomposition of copper hydroxide (Figure 11) [65].

The formation of copper oxide under hydrothermal conditions can be explained by a two-step process; firstly, copper hydroxide formed and later on, it decomposed to copper oxide:

$$Ca(OH)_2 + Cu(NO_3)_2 \rightarrow Ca(NO_3)_2 + Cu(OH)_2 \quad (2)$$

$$Cu(OH)_2 \overset{HT}{\rightarrow} CuO + H_2O \quad (3)$$

Quirino et al. [66] obtained similar results during the synthesis of copper oxide under hydrothermal conditions in microwave reactors (MHT):

$$2NaOH + Cu(NO_3)_2 \rightarrow 2NaNO_3 + Cu(OH)_2 \quad (4)$$

$$Cu(OH)_2 \overset{MHT,t=130}{\rightarrow} CuO + H_2O \quad (5)$$

The results of AAS analysis showed that after synthesis the concentration of Cu^{2+} ions in liquid medium was lower than 0.01%. The same results were obtained under all experimental conditions. Thus, it can be stated that copper ions do not participate in the reaction of calcium silicates hydrates formation but form CuO or $Cu(OH)_2$.

By prolonging the duration of isothermal curing to 4 h, the mineral composition of synthesis products remained unchanged (only the traces of copper hydroxide were not identified) (Figure 10, curve 2). Meanwhile after 8 hours of synthesis, together with semicrystalline CSH and copper oxide, the low intensity diffraction peaks characteristic to 1.1 nm tobermorite and katoite were observed (Figure 10, curve 3). In addition, after 16–72 h of isothermal curing, the traces of kilchoanite

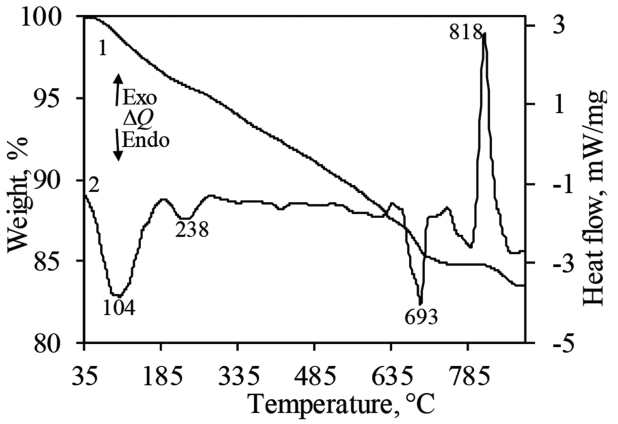

Figure 12. STA curves (1 – TG; 2 – DSC) of synthesis products obtained in the mixtures with Cu^{2+} additive, when the duration of synthesis was 24 h.

and scawtite were also identified in the synthesis products (Figure 10, curve 4).

The XRD results are in good agreement with STA data (Figure 12). In the DSC curve of synthesis products obtained after 24 h of synthesis, a clear peak at 238°C temperature, which can be assigned to the dehydration of katoite [67], was identified (Fig 12). Furthermore, there is no evidence of thermal effects in a 300–650°C temperature range. Above 650°C temperature, two thermal effects reflecting the decomposition of calcite (693° C) and recrystallization of C-S-H (I) to wollastonite (818° C) were observed (Figure 12). It was calculated that the heat (87.82 J/g) of the latter process is 4.2 times higher in a comparison with a sample with Co^{2+} ions (21.05 J/g). Probably, due to interaction between calcium oxide, silicon dioxide and cobalt ions, in the samples with Co^{2+} ions, the lower quantity of semicrystalline CSH are present.

4. Summary

By summarizing results, it can be stated, that both synthesis duration and nature of metal ions influence on the formation of the compounds in a CaO-SiO_2-Al_2O_3-H_2O system at 200°C temperature under the saturated steam pressure (Table 1). It was determined, used Cu^{2+}, Co^{2+}, and Cr^{3+} ions promote interaction between primary compounds, because in these systems portlandite fully reacted after 0 h (in systems with Cr^{3+} and Cu^{2+} ions) or 8 h (in systems with Co^{2+} ions) (Table 1), meanwhile in a pure system only after 16 h of isothermal curing (Figure 1).

It was determined that Cu^{2+}, Co^{2+}, and Cr^{3+} ions retire the formation of compounds containing aluminum ions, because in a CaO-SiO_2-Al_2O_3-H_2O system katoite ($Ca_3Al_{2.85}O_{2.55}(OH)_{9.45}$) formed after temperature increment to 200°C (Figure 1), meanwhile in the mixtures with transition metals' these compounds formed after 8–72 h of synthesis (Table 1).

Table 1. Formation and stability of compounds under hydrothermal conditions at 200°C.

Additive Duration, h	Cr^{3+}	Co^{2+}	Cu^{2+}
0	C-S-H (I) C-S-H (II)	C-S-H (I) C-S-H (II)	C-S-H (I) C-S-H (II)
4	C-S-H (I) C-S-H (II) Tobermorite	Portlandite	Copper oxide Copper hydroxide
8	C-S-H (I) C-S-H (II) Tobermorite Katoite	C-S-H (I) C-S-H (II) Kaolinite/dickite Monticellite	C-S-H (I) C-S-H (II) Copper oxide Katoite Tobermorite
16	C-S-H (I)		C-S-H (I)
24	C-S-H (II)		C-S-H (II)
48	Tobermorite	C-S-H (I)	Copper oxide
72	Katoite	C-S-H (II)	Katoite
	Scawtite	Kaolinite/dickite	Tobermorite
		Monticellite	Kilchoanite
		Kilchoanite	Scawtite
		Scawtite	
		Xonotlite	

It was obtained that in pure system semicrystalline type compounds and higher basicity (CaO/SiO_2 < 1.5) calcium silicates and calcium silicate hydrates were formed. The different results were obtained in the systems with metal ions: after 4 h of isothermal curing in CaO-SiO_2-Al_2O_3-$Cr(NO_3)_3$-H_2O and CaO-SiO_2-Al_2O_3-$Cu(NO_3)_2$-H_2O systems, lower basicity calcium silicate hydrate – 1.13 nm tobermorite ($Ca_5Si_6O_{17}(OH)\cdot 5H_2O$) were formed and remained stable under all synthesis conditions. It is worth mentioning, that tobermorite forms in the mixtures, which CaO/SiO_2 ratio varies in a 0.75–1 range and is not stable at hydrothermal synthesis temperature higher than 150°C. Further, the higher basicity calcium silicates – kilchoanite formed only in mixtures with cobalt and copper ions, after 16–48 hours.

The results of XRD and AAS analysis showed, that all investigated metal ions were intercalated into the structure of synthesis products or formed compounds because the concentration of them in the liquid medium did not exceed even 0.01%. It was determined, that Cr^{3+} ions incorporate into the structure of formed compounds because diffraction peaks characteristic to compounds containing mentioned ions were not detected in the XRD pattern. Meanwhile, Cu^{2+} and Co^{2+} ions participated in chemical reactions, consequently, copper oxide, copper hydroxide, and monticellite were formed.

Since, all investigated metal ions intercalated into the synthesis products structure or formed compounds, in the further research, the obtained with incorporated metal ions will be applied for the production of catalyst and/or adsorbents.

5. Conclusions

It was determined that at the beginning of hydrothermal synthesis (0–8 h) the intensive interaction between raw materials (CaO, SiO_2, and Al_2O_3) proceeded because in all mixtures portlandite was fully reacted and semi-crystalline type compounds C-S-H (I) and/or C-S-H (II) were formed. It was obtained the nature of used metal ions affected the formation of calcium silicate hydrates, because in systems with Cr^{3+} ions only 1.13 nm tobermorite was formed, while in systems with Cu^{2+} and Co^{2+} ions kilchoanite, 1.13 nm tobermorite or xonotlite were formed.

It was observed, all investigated metal ions were intercalated into the structure of synthesis products or formed compounds during the hydrothermal synthesis because after synthesis the metal ions concentration in liquid medium was lower than 0.01% under all experimental conditions. It was obtained that in the CaO-SiO_2-Al_2O_3-$Cr(NO_3)_3$-H_2O mixture, all chromium ions were intercalated to the structure of calcium silicate hydrates or formed amorphous structure compounds. It was determined, that after calcination of synthesis products with Cr^{3+} ions at 700°C temperature, calcium chromate was formed ($CaCrO_4$).

It was determined, that by increasing synthesis temperature up to 200°C, in the mixture with Cu^{2+} ions copper oxide formed and remained stable under all experimental conditions. The formation of copper oxide proceeded by a two-step reaction: firstly, copper hydroxide formed, which, later on, decomposed to copper oxide. It was obtained, that in the system with Co^{2+} ions, due to interaction between cobalt ions and calcium silicates, cobalt calcium silicate – monticellite ($Ca_{1.255}Co_{0.745}SiO_4$) was formed.

Compliance with ethical standards

The authors declare that there is no conflict of interest.

Disclosure statement

No potential conflict of interest was reported by the authors.

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