



Gas Formation Reactions in the Raw Mixture Based on TPP Ash

Hanna Koshlak

Kielce University of Technologies, Poland

<https://orcid.org/0000-0001-8940-5925>

corresponding author's e-mail: hkoshlak@tu.kielce.pl

Abstract: The article discusses the physicochemical mechanisms of the effect of chemical reagents on the processes of swelling of the raw mixture based on the ash of thermal power plants. The process of structure formation in such mixtures occurs as a result of physicochemical transformations of its constituent components. To intensify gas evolution and obtain materials of a porous structure, the presence of a gas former is necessary. The author has analysed the possibility of creating a porous structure in a raw mixture based on ash with the introduction of various gas formers or their formation as a result of exchange reactions. The main chemical compounds contributing to pore formation have been determined. To form a given structure, it is proposed to control chemical transformations at the stage of swelling. To study the processes of intensification of gas evolution, the author proposes to investigate the mechanisms of the influence of mineral fillers and chemical reagents on swelling processes based on the analysis of the Gibbs equation. The parameters of the Gibbs equation are obtained, by which it is possible to determine the probability of the occurrence of chemical reactions with the proposed chemical agents for the formation of gas bubbles with (pores) in the raw material.

Keywords: swelling, porous structure, ash of thermal power plants

1. Introduction

As a result of coal combustion at thermal power plants, a large amount of ash and slag waste is generated. The level of this waste disposal in Russia is about 4-5%; in developed countries – about 50%, in France and Germany – 70%, and in Finland – about 90% of their total amount (Lee et al. 2020). These countries use mainly dry ash, their disposal is encouraged by the national policy. Nowadays, the problem of ash and slag waste is becoming more acute, as it is generated in large volumes and have an utterly negative environmental impact. The waste accumulates in rising volumes, resulting to a rapid increase in environmental, social and economic costs due to the extremely low disposal level. Moreover, due to their physicochemical and physical composition, these materials



are considered as unique resources to be used in various economic sectors with significant social, environmental and economic effects (Bielecka et al. 2020).

One of the possible solution to a problem is the development and implementation of effective thermal insulation porous materials based on ash containing raw mixture. Abundance of raw materials, relatively simple technology, low capital production costs, as well as attractive thermophysical characteristics could ensure wide use of these porous materials in industry. To ensure production of energy-efficient materials, features of the raw mixture swelling shall be studied in detail. Consequently, the production technology of ash-based porous thermal insulation structures shall be solved by studying the mechanism of a porous structure formation as a result of chemical reactions.

There are three main approaches to the elementary porous system formation. The first one considers the porous structure formation during a pseudo-continuous medium dispersion resulting from sublimation, condensation, crystallization and chemical reactions. The second approach is a porous system growth by adding porous systems of a smaller spatial scale (colloidal systems, bulk materials, etc.). There is an approach, where porosity is considered as fine-structure three-dimensional defects (metals, alloys, certain minerals). There is also a combined approach to a porous system formation, analysing more complex porous systems and their combinations (building materials, foam glass, insulation materials).

A porous system can be formed by diffusion accumulation of gases (diffusion genesis) and material destruction (destruction genesis). Diffusion accumulation of gases is a pore formation process during the release of gases in the material as a result of chemical reactions, difference in a substance saturation with gases in different physical states, transition to the gaseous state of one of the initial mixture components. The mechanism of a porous structure formation as a result of chemical reactions is based on the release of gases, accumulating in the least dense locations and forming gas bubbles. If the pressure in gas bubbles is higher than the sum of external and hydrostatic pressure, the liquid mixture of material boils. To intensify the pore formation process, the pressure is considerably reduced and the mixture starts boiling.

The formation of gases is also possible as a result of transition of one of the mixture components in the gaseous physical state (Pavlenko et al. 2019). At this, there gas accumulates and a pore is formed under the internal pressure action. Diffusion genesis also includes pore formation resulting from difference in the substance saturation in its solid and liquid state. Gas solubility in a liquid medium is higher than in a solid one. Therefore, dissolved gases are displaced during solution crystallization. If the solution surface has already crystallized, then an excess gas begins to accumulate upstream crystallization front, then it moves along with the crystallization front until its concentration exceeds the

maximum possible concentration of dissolved gas in the solution. In all these cases of diffusion genesis (pore formation as a result of chemical reactions, difference in gas saturation of the substance in different physical states, resulting from evaporation of one of the initial mixture components) pore nucleation and its growth rate are the most important issues (Pavlenko et al. 2014). Although the pore nucleation location is fluctuating, the most viable pore nuclei are formed near structural imperfections. Such imperfections include the interface of different chemical structures, different physical states of one element; pores and cavities, formed as a result of the material destruction. In a liquid physical state, such imperfections diffuse in volume and can merge. To merge pore nuclei, energy shall be spent on the structure deformation.

2. Purpose of work and research methods

It is evident that ash shall not be considered as the industrial waste, but as a resource for production of new materials. One of TPP ash disposal methods is to use it in the technology of porous thermal insulation material production by means of thermal swelling of water soluble mineral raw mixture. To solve this task it is necessary to study main physico-chemical processes and transformations in the ash structure.

The structure in a mixture is formed as a result of physico-chemical transformations of ash components. Thermal swelling, the main process of structure formation and pore nuclei formation as its initial stage, result from chemical reactions in the mixture.

One of TPP ash disadvantages is its inconstant composition, depending on morphological characteristics of the burning fuel, milling fineness during its preparation, fuel ash-content, chemical composition of the fuel mineral part, temperature in the burning area, period of particles presence in this area, etc. Moreover, the ash, stored in ash dumps, is under constant chemical transformations, resulting in gradual change of its chemical composition.

TPP ash chemical composition was studied to determine its possible use as a raw material for production of building materials. According to standard modern methods, ash chemical composition is determined, it is presented in Table 1. Use of ash in its pure form is complicated by the negative impact of CaO (calcium (II) oxide), present in a free form in the burnt state. Hydration of CaO particles, often coated with a glassy shell, results in cracking and destruction of solidified material. The harmful impact of CaO can be neutralized by different means: physical, chemical and its use with cement. The positive effect in the latter case will be achieved as a result of dilution and containment of destructive phenomena using a set cement.

Table 1. Average content of TPP ash components

Substance	Formula	Content, wt.%
Silicon (IV) oxide	SiO ₂	52.08
Aluminium (III) oxide	Al ₂ O ₃	26.58
Iron (III) oxide	Fe ₂ O ₃	13.0
Magnesium (II) oxide	MgO	2.4
Calcium (II) oxide	CaO	4.13
Manganese (II, III) oxide	Mn ₃ O ₄	0.3
Titanium (IV) oxide	TiO ₂	0.84
Chromium (III) oxide	Cr ₂ O ₃	0.003
Sulfur (VI) oxide	SO ₃	0.38
Phosphorus (V) oxide	P ₂ O ₅	0.23
Potassium oxide	K ₂ O	1.5
Sodium oxide	Na ₂ O	0.5
Bound water	H ₂ O	0.2
Carbon (IV) oxide	CO ₂	0.33
Calcination losses (at t = 950°C)	–	3.77

We analysed both methods in our work. As calcium oxide (CaO) content in ash is low (\approx up to 4%), each method may be relevant. During TIM production, to intensify gas emission we shall use NaOH alkali, which can be formed as a result of metabolic reactions. In our technologies alkalis can be added to the raw mixture as a separate component, its gradual formation is also possible in intermediate chemical reactions in the ash-based raw mixture. It would make it possible to control chemical transformations at the swelling stage. Formation of new compounds will promote a faster mixture plastification and its early consolidation. These properties can serve as a basis of a controlled process for a specified structure formation, which (as specified in the first section) is the purpose of this study.

Therefore, interaction of these chemical compounds accelerates CaO hydration, as well as formation of mixture hydrates.

Complex physicochemical and chemical processes in the interaction of clinker minerals with water occur according to the following equations:

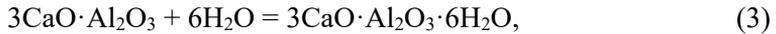
- C₃S tricalcium silicate hydrolysis



- C₂S dicalcium silicate hydration



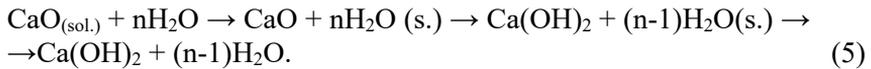
- C₃A tricalcium aluminate hydration



- C₄AF tetracalcium (four-calcium) aluminoferrite hydrolysis



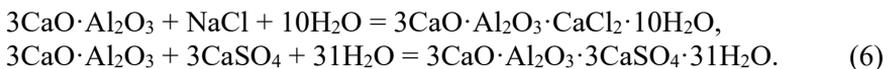
The presence CaO compound in the system, which is in a free state, affects strength properties of the final product. During hydration with CaO transformations occur according to the following pattern:



If the process takes place in the absence of excess water, then Ca(OH)₂ crystallizes rapidly and inside formed compound particles there is an increased internal stress, resulting in mixture cracking. To eliminate destructive phenomena in the cement, chemical additives are introduced into the mixture.

The solubility promoting compounds accelerate the swelling process and form soluble compounds with CaO: NaCl, CaCl₂, MgCl₂, NH₄Cl, Ca(NO₃)₂. Additives, slowing down CaO activity and forming sparingly soluble compounds on its surface, that prevent water access: CaSO₄ · 2H₂O, Na₂SO₄. Chemical additives react with cement minerals, forming complex compounds: calcium hydrosulfoaluminates and hydrochloroaluminates 3CaO·Al₂O₃·3CaSO₄·nH₂O, 3CaO·Al₂O₃·nCaCl₂·mH₂O. These compounds increase the active surface of cement grains, the rate of cement interaction with water and strengthen a set cement.

The ash CaO interacts with portland cement clinker according to the following metabolic reactions:

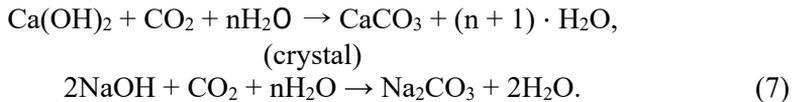


The strength of ash-containing concrete depends on the chemical and mineralogical composition of a cement clinker. At an early growth state, the concrete strength is facilitated by the increased content of alkali in the clinker, accelerating ash and cement chemical interaction (Poletini et al. 2009). Additives, such as CaCl₂ and CaSO₄, can be used to activate ash for use in cement systems (Poon et al. 2001). Addition of sodium chloride (NaCl) to a cement mixture in the amount of 1.2-1.5% promotes CaO hydration (Bellmann 2009).

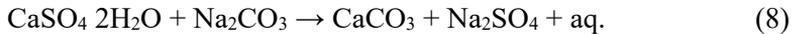
U. A. Ayapov (Ayapov 1982) proposed to add sodium sulfate into the mixture (Na₂SO₄), which affects structure formation processes in a lime-ash binder system. The presence of a high content of Al₂O₃ in a system (18-24 wt.%), results in a shift of ionic equilibrium towards formation of sparingly soluble ettringite – calcium hydrosulfuminate (3CaO·Al₂O₃·3CaSO₄·nH₂O). It increases alkaline

environment as a result of formation in a sodium hydroxide (NaOH) system, which enhances the effect of ash sulfate-alkaline activation, namely the destruction of Si-O-Al bonds, while ettringite crystals contribute to destruction of Si(OH)₄ (OH) and Al(OH)₃ gel colloidal film; chemical reactions accelerate on the ash grains surface, they are further enhanced by curing.

As a result of exchange reactions between sodium sulfate and cement hydration products, an additional amount of sulfate crystal hydrates is formed – gypsum (CaSO₄·2H₂O) and alkali NaOH. When Portland cement sets in the air, it results in carbonization due to carbon (IV) oxide (CO₂) (concentration 0.03%)

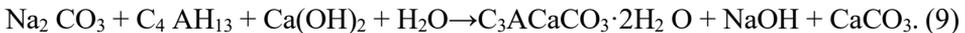


Disodium trioxocarbonate (Na₂CO₃) interacts with gypsum first, as it is the most soluble product of Disodium trioxocarbonate (Na₂CO₃) hydration, under the action of NaOH, its solubility increases considerably:



Highly soluble in water sodium sulfate reacts again with calcium oxide to form gypsum and alkali.

The simplest way to increase the water resistance of a set cement is possible to be used with the introduction of additives of electrolyte salts, when additional crystal hydrates are formed. Salts-electrolytes (e.g. NaNO₃, Na₂SO₄, Na₂CO₃, dissolving in water, penetrate deep into the concrete structure and react with components of a set cement solidification products. Use of salts results in their interaction with a set cement components with formation of AFt and AFm phases and hydrosilicates. The mechanism of Na₂CO₃ (disodium trioxocarbonate) action can be represented as its reaction with calcium hydroaluminat in the presence of calcium hydroxide, followed by the formation of two sparingly soluble products, one of which is represented by a double salt:



A simple exchange reaction is also possible:



Carbonization occurs in the surface layer. Formed CaCO₃ increases in volume and promotes strengthening of the outer concrete surface. Gradually, the system activates surface self-compaction processes with spontaneous slowing down of the carbonization phenomenon, resulting in a dense surface formation, it prevents CO₂ (carbon (IV) oxide) access, which is part of the air, into deep layers.

As ash contains up to 61% of aluminosilicate glass phase, similar reactions of interaction with Na_2SO_4 (sodium sulfate) will take place in ash-cement compositions. It is an obvious benefit, as theoretically we can influence kinetic parameters of the swelling process. Moreover, carbonized shrinkage during product carbonized shrinkage will partially compensate for their own expansion deformations by free lime quenching.

3. Experimental research

The impact mechanisms of mineral fillers and chemical reagents on swelling processes may be evaluated based on analysis of the combined equation of the first and second laws of thermodynamics.

$$\Delta G = P \cdot \Delta V + \sigma \cdot \Delta F + \mu \cdot \Delta n + \varphi \cdot \Delta q - T \cdot \Delta S = \Delta H - T\Delta S, \quad (11)$$

where:

ΔG – Gibbs free energy allowing prediction of intensity and direction of changes in the system energy state,

ΔH – system enthalpy factor,

σ – the surface tension at the pore interface,

F – the pore surface area,

n – the rate of a volume change,

φ – the chemical potential of a pore-forming gas,

$T\Delta S$ – an entropy factor.

The entropy factor changes with porous structure formation with the following work, performed by the system (a raw mixture):

- change of system volume,
- formation of a new surface and increase of surface tension during frame hardening,
- change of chemical potential, phase and component composition.

The entropy factor increases as a result of the porous structure formation, using technological techniques, described in the previous chapters.

Gibbs energy is represented by the following equation

$$G^{(1)} = \varphi M^{(1)} + \sigma\Omega, \quad (12)$$

where: $M^{(1)}$ is the mass of a pore forming agent equal to $4\pi r^3/\nu'$,
 Ω is the outer surface of a pore nucleus, $4\pi r^2$,
 φ is the chemical potential of a pore-forming gas.

Gibbs energy of a system, consisting of the energy of a pore nucleus formation and a material porous structure

$$G = G^{(1)} + G^{(2)}, \quad (13)$$

where $G^{(2)}$ is Gibbs energy of the material.

Let us analyse the equilibrium state of this system. If system external pressure p' , equal to gas pressure in a pore and temperature T' are constant, then equilibrium condition $dG = 0$ is represented by

$$dU^{(1)} + dU^{(2)} - T'(dS^{(1)} + dS^{(2)}) + p'(dV^{(1)} + dV^{(2)}) + \varphi^{(1)}dM^{(1)} + \varphi^{(2)}dM^{(2)} = 0, \quad (14)$$

where: U is internal energy; p' is external pressure (in this case mixture pressure).

Considering that

$$\left(\frac{\partial U}{\partial S}\right)_V = T; \quad \left(\frac{\partial U}{\partial V}\right)_S = -p, \quad (15)$$

for a gas bubble according to Laplace formula

$$p^{(1)} = \left(p' + \frac{2\sigma}{r}\right), \text{ then} \\ dU^{(1)} + dU^{(2)} = T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)} - \left(p' - \frac{2\sigma}{r}\right)dV^{(1)} - p'dV^{(2)}. \quad (16)$$

Considering that the system total mass is constant

$$\frac{2\sigma}{r}dV^{(1)} + \left(\varphi_{\infty}^{(1)} - \varphi^{(2)}\right)dM^{(1)} = 0. \quad (17)$$

For spherical pores

$$dV^{(1)} = 4\pi r^2 dr, \quad (18)$$

$$dM^{(1)} = \frac{4\pi r^2}{\nu^{(1)}} dr. \quad (19)$$

The above ratio can be written as

$$\left(\varphi_{\infty}^{(1)} - \varphi^{(2)} + \frac{2\sigma v^{(1)}}{r}\right) dr = 0 \quad (20)$$

or under condition $dr \neq 0$,

$$\varphi^{(2)} - \varphi_{\infty}^{(1)} = \frac{2\sigma v^{(1)}}{r}. \quad (21)$$

Let us assume instead $\varphi_{\infty}^{(1)}$ and $\varphi^{(2)}$ actual values of the pore-forming agent and material chemical potentials at a specified temperature and corresponding pressure equal to $\varphi^{(1)}(p^{(1)}, T)$, $\varphi^{(2)}(p^{(2)}, T)$. Similarly to a gas bubble in an infinite volume of liquid, decomposing $\varphi^{(1)}(p^{(1)}, T)$ in a row by $p^{(1)} - p^{(2)}$, and $\varphi^{(2)}(p^{(2)}, T) - \varphi^{(1)}(p^{(1)}, T)$ in a row by orders $p^{(2)} - p^{(1)}$. We will obtain

$$\varphi^{(1)}(p^{(1)}, T) = \varphi^{(2)}(p^{(2)}, T). \quad (22)$$

From equation (22) it follows that the pore-forming agent and material chemical potentials have equal values. Thus, conditions of gas pressure equilibrium in the material during porous structure formation, taking into account the surface tension:

$$\{T^{(1)} = T^{(2)}, p^{(1)} - p^{(2)} = \frac{2\sigma}{r}, \varphi^{(1)}(p^{(1)}, T) = \varphi^{(2)}(p^{(2)}, T)\}. \quad (23)$$

After differentiation of equation (11) by pressure p at $T = const$ and given that $(\partial\varphi/\partial p)_T = v$, we obtain

$$\frac{1}{\rho^{(2)}} - v^{(1)} = -\frac{2v^{(1)}\sigma}{r^2} \left(\frac{\partial r}{\partial p}\right)_T + \frac{2\sigma}{r} \left(\frac{\partial v^{(1)}}{\partial p}\right)_T. \quad (24)$$

As $\frac{1}{\rho^{(2)}}$ is much lower than $v^{(1)}$, and $v^{(1)}$ at relatively low gas pressures can be considered equal to RT/p , then

$$\frac{RT}{p^{(1)}} = \frac{2v^{(1)}\sigma}{r^2} \left(\frac{\partial r}{\partial p}\right)_T - \frac{2\sigma}{r} \left(\frac{\partial v^{(1)}}{\partial p}\right)_T. \quad (25)$$

After integrating this equation by $p \geq 0$ we obtain

$$\int \frac{RT}{p^{(1)}} dp = \int \frac{2v^{(1)}\sigma}{r^2} \left(\frac{\partial r}{\partial p}\right)_T dp - \int \frac{2\sigma}{r} \left(\frac{\partial v^{(1)}}{\partial p}\right)_T dp, \quad (26)$$

$$RT \cdot [\ln \ln (p^{(1)}) + c] = -2\sigma \frac{v^{(1)}}{r}, \quad (27)$$

where c is the integration constant.

$$p^{(1)} = e^{-c} \cdot e^{-\frac{2\sigma v^{(1)}}{RT r}}$$

We obtain constant e^{-c} from equilibrium condition, given that at $r \rightarrow \infty$, $p = p_0$:

$$p^{(1)} = p_0 \cdot e^{\frac{2\sigma v^{(1)}}{RT} \frac{1}{r}}. \tag{28}$$

After differentiating the equation of equality of potentials (23) by T and given that $(\partial\varphi/\partial p)_T = v$, $(\partial\varphi/\partial T)_p = -S$ we obtain

$$\left(\frac{\partial\varphi^{(1)}}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial\varphi^{(1)}}{\partial T}\right)_p = \left(\frac{\partial\varphi^{(2)}}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial\varphi^{(2)}}{\partial T}\right)_p, \tag{29}$$

$$dT = \frac{I}{s^{(2)} - s^{(1)}} \left(\frac{I}{\rho^{(2)}} \cdot dp^{(2)} - v^{(1)} \cdot dp^{(1)} \right). \tag{30}$$

As the material density is almost independent of the pressure at low gas pressures $v = RT/p$, we obtain

$$T = \frac{I}{s^{(2)} - s^{(1)}} \left(\frac{p^{(2)}}{\rho^{(2)}} - RT \ln|p^{(1)}| \right) + const. \tag{31}$$

Given $P = const$, $(\partial\varphi/\partial T)_p = -s$, we finally write

$$s^{(1)} - s^{(2)} = \frac{2\sigma v^{(1)}}{r^2} \left(\frac{\partial r}{\partial T} \right)_p + \frac{2\sigma}{r} \left(\frac{\partial v^{(1)}}{\partial T} \right)_p, \tag{32}$$

$$s^{(2)} - s^{(1)} = -\frac{2\sigma v}{rT}.$$

Considering (30):

$$T = \frac{I}{R \ln|p^{(1)}|} \cdot \left(\frac{2\sigma v^{(1)}}{r} + \frac{p^{(2)}}{\rho^{(2)}} \right). \tag{31}$$

At $r \rightarrow \infty$ we obtain

$$\Delta T = \frac{I}{R \ln|p^{(1)}|} \cdot \left(\frac{2\sigma v^{(1)}}{r} + \frac{p^{(2)}}{\rho^{(2)}} \right) - T_0, \tag{32}$$

where T_0 is a pore forming gas temperature.

Thus, all parameters for equation (11) are obtained, it is possible to determine probable chemical reactions and formation of gas bubbles (pores) in a raw material.

4. Conclusions

To intensify gas evolution in a mixture based on ash, the presence of a gas former is necessary, which can be formed as a result of exchange reactions. In ash and slag materials, the chemical and mineral-phase composition depends on the composition of the mineral part of the fuel, its calorific value, the combustion mode, the method of catching and removing incineration waste, and the place where raw materials are taken from the dumps. The use of additional gasifiers in certain technological modes contributes to the implementation of an intensive and controlled process of emission gases (for pore formation in the plastic raw material mixture). The mechanisms of the effect of mineral fillers and chemical reagents on the swelling processes can be estimated based on the analysis of the Gibbs equation, which makes it possible to predict the intensity and direction of changes in the energy state of the system. It will make it possible to determine the quantitative composition of a raw mixture with TPP ash addition and main technological modes of its swelling. The obtained results can be used to quantify components of a raw mixture for production of porous structures and perform further research to optimize the composition and technological modes of swelling.

References

- Ayapov, U.A. (1982). Binders and concretes from mineral wastes of the industry of Kazakhstan /U.A. Ayapov S.A. Arkhabaev, Z.B. Shormanova. - A.: Nauka, 164.
- Bellmann, F., Stark, J. (2009). Activation of blast furnace slag by a new method. *Cem. Concr. Res.*, 39, 644-650.
- Bielecka, A., Kulczycka, J. (2020). Coal Combustion Products Management toward a Circular Economy – A Case Study of the Coal Power Plant Sector in Poland. *Energies*, 13, 3603.
- Koshlak, H., Pavlenko, A. (2019). Method of formation of thermophysical properties of porous materials. *Rocznik Ochrona Srodowiska*, 21(2), 1253-1262.
- Lee, J., Kim, T., Sung, M., Vu, H.H.T., Shin, K.N., Ahn, J.W. (2020). An Integrative Approach to International Technology Transfer for Recycling Vietnam Coal Ash with Consideration of the Technological, Legal, and Network Perspectives. *Sustainability*, 12, 771.
- Pavlenko, A., Koshlak, H. (2019). Heat and mass transfer during phase transitions in liquid mixtures. *Rocznik Ochrona Srodowiska*, 21(1), 234-249.
- Polettini, A. (2009). Chemical Activation in View of MSWI Bottom Ash Recycling in Cement-Based Systems/A. Polettini, R. Pomi, E. Fortuna. *J. Hazardous Matter*. 162(2-3), 1292-1299.
- Poon, C.S. (2001). Activation of fly ash/cement systems using calcium sulfate anhydrite (CaSO₄)/C.S. Poon, S.C. Kou, L. Lam, Z.S. Lin. *Cem. And Concr. Res.* 31(6), 873-881.