

## Problem of Impurity of Salts of Alkali Metals in Cement Raw Materials

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**Abstract:** In this work the problem of impurity of salts of alkali metals in the cement raw materials, possessing tendency to accumulate in the oven unit as a result of sublimation (evaporation) and therefore causing technological violations is considered. The comparative analysis of ability of chlorides, sulfates and carbonates to transform into a gas phase from a burned material is carried out at high temperatures and also extent their influence on processes of mineral formation and quality of cement. The main importance of chlorides in formation of outgrowths (sows) in flues of the cyclonic heat exchanger is demonstrated by their indirect impact on hydration activity of clinker.

**Key words:** Salts of alkali metals • Sublimation • A clinker microstructure • Quality of cement • Formation of sows (outgrowths) in the cyclonic heat exchanger

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### INTRODUCTION

Compounds of alkali metals are widespread impurities in raw materials for production of cement. Due to the high volatility they are sublimated at high-temperature and condensed in cold part of oven system and circulating many times collect in a burned material [1-3]. Concentration of alkali impurities in materials being in oven system can sometimes reach 5–13% and, therefore, surpass the total content of the main  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  oxides having the considerable impact on technological processes and clinker [4] synthesis. On the one hand, they are mineralizers, accelerating the cold processes of a Clinker formation and on the other hand they are inhibitors of high-temperature processes complicating synthesis of alite.

According to the experience of cement works [5-7], impurities of compounds of alkali metals in raw materials lead to the considerable violations of process of clinker burning resulting in formation of outgrowths and sows in chain and cyclonic heat exchangers (Fig. 1).

Outgrowths contain the significant amount of water-soluble sulfates and chlorides of alkali metals whereas in an original raw materials concentration of  $\text{SO}_3$  can be ~3.5 times lower and chlorine ions – 220 times. Therefore, chlorides of alkalis possess the greatest tendency to sublimation and accumulation. Except alkaline salts and raw material components spurrite is present in outgrowths  $(2\text{CaO}\cdot\text{SiO}_2)_2\cdot\text{CaCO}_3$  reinforcing these formations. Thus, the study of action of 3% alkaline salts on  $\text{CaCO}_3\text{--SiO}_2$  system (Fig. 2) at  $760^\circ\text{C}$  shows that only KCl is an intensifier of early formed spurrite. At the high When the content of  $\text{SO}_3$  in fuel is high silicate sulfate of calcium  $(2\text{CaO}\cdot\text{SiO}_2)_2\cdot\text{CaSO}_4$  is formed and concentration of  $\text{SO}_3$  in outgrowths increases in comparison with an original raw material more than by 100 times.

It results in the increased ability of chlorides to accumulate in a material and specific mineral formation in the low-temperature area at their presence. In this regard, definition of features of physical and chemical processes of cement clinker burning under the influence of chlorides of alkali metals when their concentration is changed is a main goal of this work.

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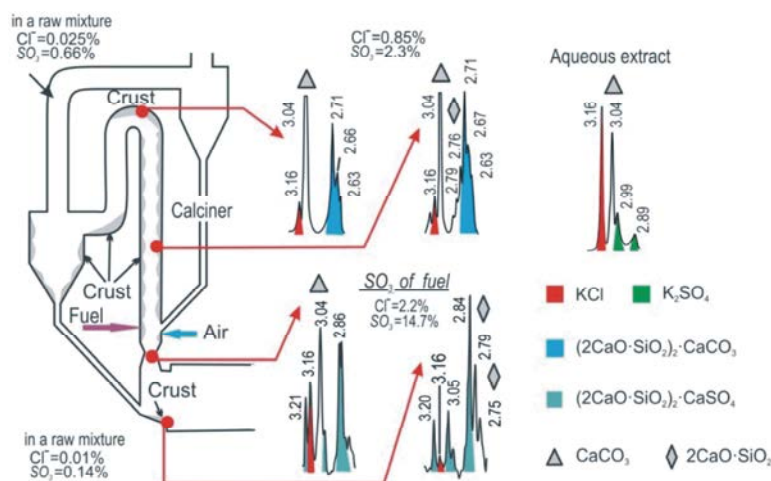


Fig. 1: Phase composition of sows in the oven unit of a dry process of production

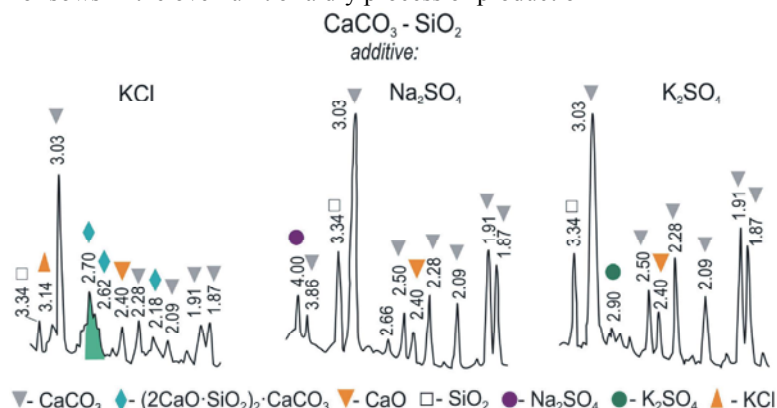


Fig. 2: Formation of spurrite in  $\text{CaCO}_3\text{--SiO}_2$  system in  $\text{CO}_2$  at  $760^\circ\text{C}$  only with KCl additive

**Technique:** In this study mixtures of chemically pure reactants, a raw mixture, clay, clinker and sows taken from various sites of production furnaces were applied. For research of transformations in  $\text{RCl--CaCO}_3$  system where  $\text{R} = \text{K}$  or  $\text{Na}$ , mixtures were prepared from chemically pure reactants mixing components by a rubber pestle for 20 minutes. KCl and NaCl salts were added in raw mixture in the form of solution with the subsequent drying and averaging for 2 hours. All materials were crushed before passing a sieve with the hole size of 80 microns.

During the investigation the thermodynamic calculations were used and the results of which were experimentally checked by X-ray phase, mass-spectrometer and complex thermal analyses. Transformations of materials during heating were investigated on high-precision installation – a differential scanning calorimeter (DSC) of the NETZSCH latest modification and MOM derivatograph. Physical and

chemical processes in  $\text{RCl--CaCO}_3$  system before and after melting were studied by a method of complex thermal analysis at the various fractional pressure of  $\text{CO}_2$  created by various amount of calcium carbonate. The gas phase formed by heating of patterns to  $1450^\circ\text{C}$  was identified by the quadrupole mass spectrometer combined with DSC.

The chemical analysis of materials was carried out by the standard methods and x-ray spectrometer. The phase composition of input products and burned products was defined by the X-ray phase analysis made by the DRON-3 installations and the petrographic analysis in reflected light made by the universal NU-2 polarizable microscope of Karl Zeiss Jena firm.

Physicomechanical tests were carried out in small cubic patterns with a size of edge of 1,41 cm in the cement paste at  $\text{B/C} = 0,28$  with the subsequent recalculation according to the standard conditions for what durability of a control cement specimen with the Russian Standart stated activity was defined as well.

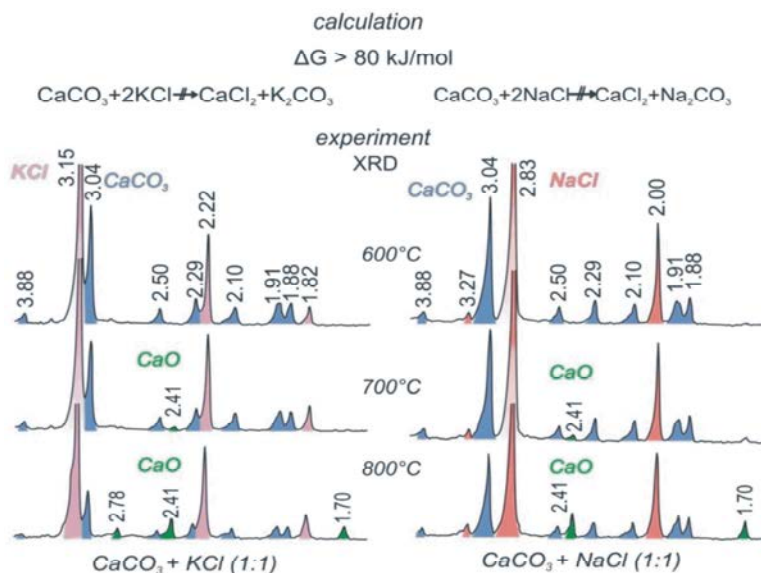
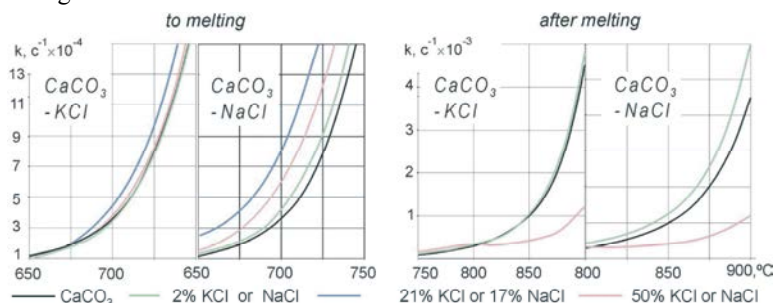


Fig. 3: Possibility of exchange reactions

Fig. 4: Influence of various concentration of KCl and NaCl on the process of  $\text{CaCO}_3$  decompositionTable 1: Efficient activation energy  $E$  and the value of preexponential multiplier  $A$  of the process of decomposition of calcium carbonate in  $\text{RCl}-\text{CaCO}_3$  system

Conditions of the experiment	Concentration, masses% RCl	E, kJ/mol		A, $\text{C}^{-1}$	
		KCl	NaCl	KCl	NaCl
Before forming a melt (15 mg of $\text{CaCO}_3$ )	0	225		$5.01 \cdot 10^8$	
	2	235	218	$1.64 \cdot 10^9$	$2.18 \cdot 10^8$
	10*	234	205	$1.85 \cdot 10^9$	$0.85 \cdot 10^8$
	50	228	214	$0.78 \cdot 10^9$	$2.05 \cdot 10^8$

\*10 masses% on chlorine that corresponds to 21% of KCl and 17% of NaCl

Interactions in RSL mixtures –  $\text{CaCO}_3$  and  $\text{RCl}$  – clay  
 First of all interaction of chlorides of alkali metals with a prevailing component of a raw mixture – calcium carbonate was investigated.

By thermodynamic calculations (Fig. 3) and the X-ray phase analysis (XRD) it is established that chlorides of a potassium and sodium do not form with calcium carbonate the steady products of an exchange reaction that is proved by [8].

However before melting alkaline chlorides intensify process of a decarbonization of  $\text{CaCO}_3$ , destabilizing its lattice, with the increase of their concentration to the particular limit corresponding to 10% for  $\text{Cl}^-$ , i.e. 21% of

KCl and 17% of NaCl that can be seen on the kinetic curves of decomposition of  $\text{CaCO}_3$  based on the results of a complex thermal analysis (Fig. 4).

Moreover NaCl affects  $\text{CaCO}_3$  lattice more actively. According to the Arrhenius equation, intensifying effect of cation of sodium can be explained by the decrease in activation energy  $E$  and potassium cation – by the increase in a preexponenta  $A$  (Table 1).

With the formation of the considerable quantity of a melt the speed of  $\text{CaCO}_3$  dissociation rapidly decreases, in ~ 4 times due to the increase of fractional  $\text{CO}_2$  pressure because of need to overcome the surface intention of a film of the formed melt.

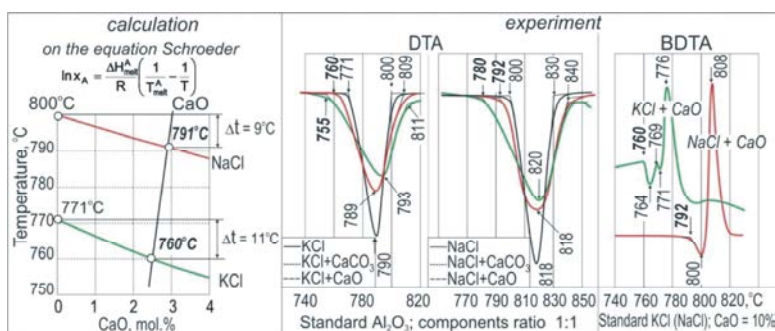


Fig. 5: Experimental determination of temperature of eutectics in RCl– CaO and RCl – CaCO<sub>3</sub> systems by DTA and bidifferential-thermal analysis (BDTA)

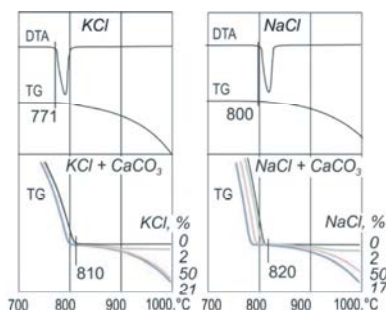


Fig. 6: Change of temperature at the beginning of intensive evaporation of chlorides of alkalis at the presence of CaCO<sub>3</sub>

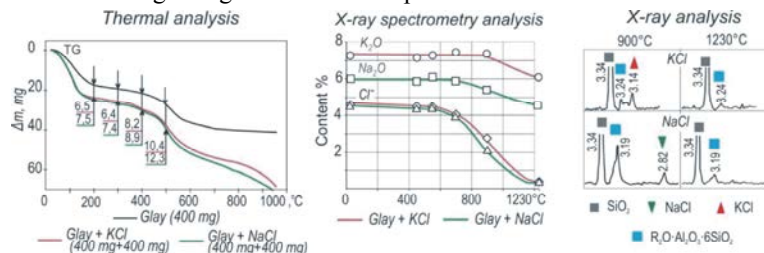


Fig. 7: KCl and NaCl interaction with clay with the formation of aluminosilicates of alkali metals and removal of Cl<sup>-</sup>

Formation of a melt in RCl– CaO mixtures is observed below melting points of pure KCl and NaCl as a result of formation of eutectics in binary RCl– CaO of structures 97.5 mole% of KCl and 2.5 mole CaO% at 760°C and 97.1 mole% NaCl and 2.9 mole% CaO at 792°C and in the triple RCl–CaCO<sub>3</sub>–CaO system at 755°C with KCl and 780°C with NaCl. It is confirmed by thermodynamic calculations by Schroder equation the curves of liquidus of RCl– CaO system both experimentally differential - thermal (DTA) and bidifferential-thermal analyses (BDTA) (Fig. 5) as well as the temperature increase of intensive sublimation (evaporation) of alkaline chlorides from a mixture with CaCO<sub>3</sub> (Fig. 6) as a result of a pressure decrease of a saturated steam solvent with the increase of the solved substance.

As a result of interaction of chlorides of a potassium and sodium with clay minerals alkaline aluminosilicates with Cl extraction (Fig. 7) are formed.

It occurs during dehydration due to Hedvall effect when structural change of clays and actions of water vapor are observed and more intensive loss of the weight (TG) in the presence of RCl at all stages of dehydration process is the best proof of it.

#### Influence of Chlorides of Alkali Metals on a Clinker

**Formation:** To define the specifics of the influence of chlorides on a clinker formation the complex thermal analysis of cement raw mixtures with additives of 4%Cl<sup>-</sup> in the form of KCl and NaCl to 1450°C in the neutral argon environment with simultaneous definition of a gas phase by the quadrupole mass spectrometer combined with a differential scanning calorimeter (DSC) was carried out.

It is established that in a raw mixture at the stage of clay dehydration especially above 400°C, alkaline chlorides intensify interaction of clay and carbonaceous components with formation of spurrite which is proved by

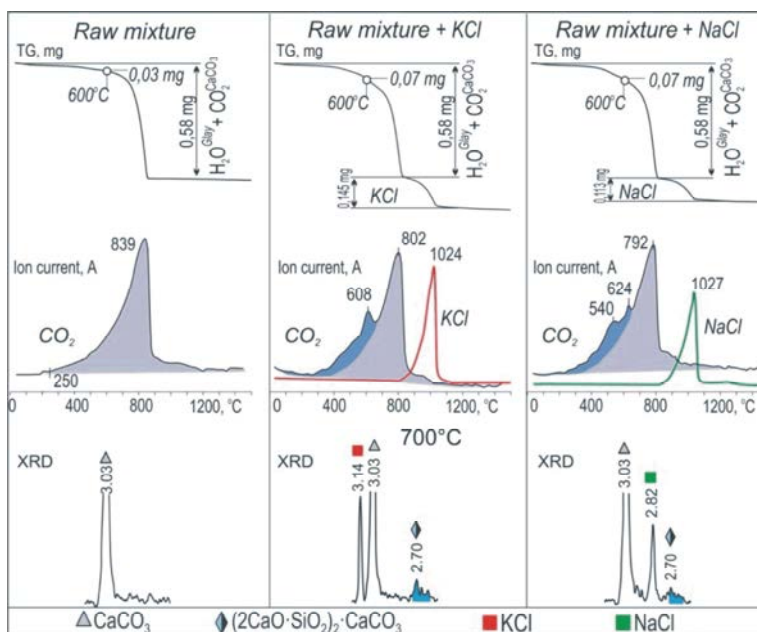


Fig. 8: Influence of the additive of 4%  $\text{Cl}^-$  in the form of KCl and NaCl in a raw mixture on clinker formation processes (KCl and NaCl evaporation speed of weight loss)

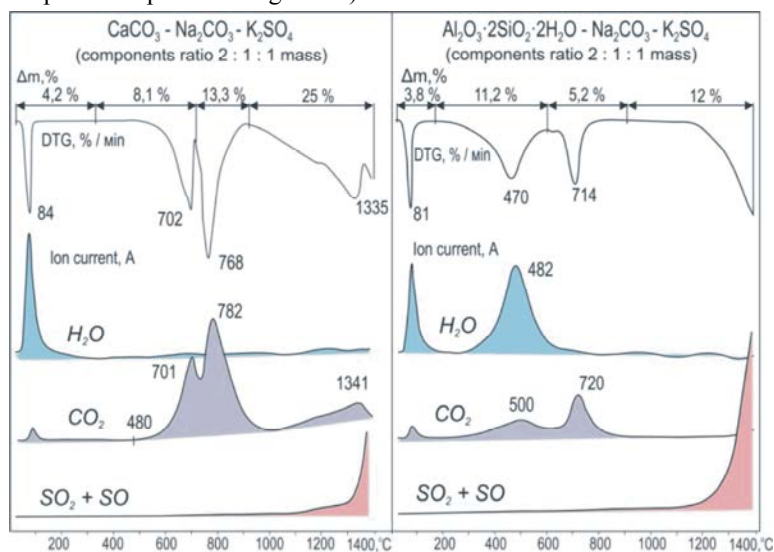


Fig. 9: Results of the mass-spectrometric analysis combined with thermogravimetric TG and differentially thermogravimetric DTG analyses of the alkali containing systems in the neutral argon medium

mass-spectrometric analysis of a gas phase formed, intensive  $\text{CaO}_2$  extraction in this interval and the X-ray phase analysis as well (Fig. 8). Sublimation of alkaline chlorides from a raw mixture begins as it was shown above with calcium carbonate after its decomposition and finishes at  $1200^\circ\text{C}$ . Chlorides pass into a gas phase almost completely without decomposition [9].

On the basis of the mass-spectrometric analysis combined with DSC, it is established that, unlike chlorides, carbonates and sulfates of alkali metals in

the course of sublimation from mixtures with  $\text{CaCO}_3$  and kaolinite are capable to decompose partially with extraction of carbon oxide and oxides of sulfur (Fig. 9).

Thus, up to  $1400^\circ\text{C}$  in a mixture with  $\text{CaCO}_3$  practically all  $\text{Na}_2\text{CO}_3$  is sublimated and the larger part of  $\text{K}_2\text{SO}_4$  remains in a material. From a mixture with kaolinite all carbon oxide is removed from  $\text{Na}_2\text{CO}_3$  and about 50% from  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{O}$  and a part of  $\text{K}_2\text{O}$  combine with aluminosilicates.



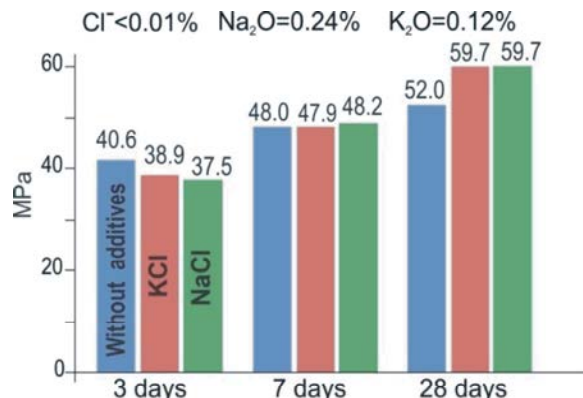


Fig. 10: Influence of the additive of KCl and NaCl in a raw mixture on the activity of clinker

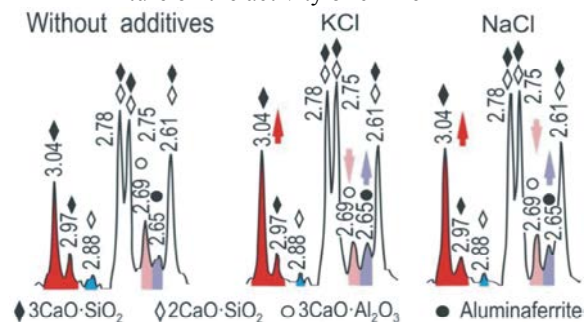


Fig. 11: Influence of KCl and NaCl on phase composition of the clinker burned at 1450°C

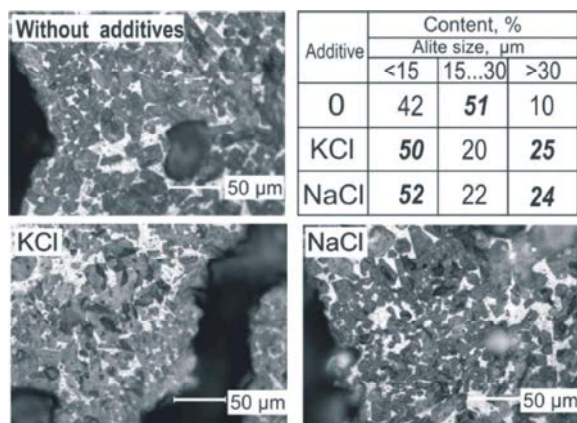


Fig. 12: Ratio of large and small alite crystals in clinker in dependence because of RCl additive in a raw mixture

Thus, negative influence of carbonates and sulfates of alkali metals on quality of clinker can be explained by their low ability to sublimate due to which they influence on all processes of clinker formation making synthesis of the main brick mineral alite very difficult. Chlorides of alkali metals almost completely evaporate from a material prior to the beginning of alite formation.

For the decrease in circulation of alkaline salts bypassing of some amount of furnace gases with their subsequent cleaning and rational use of alkali containing oven dust [10–12] is recommended.

**Influence of KCl and NaCl on Quality of Cement:** Clinkers on the basis of raw mixtures from 4% of  $\text{Cl}^-$ , burned at 1450°C and matured for 40 minutes, contain only 0.12% of  $\text{K}_2\text{O}$ , 0.24% of  $\text{Na}_2\text{O}$  and less than 0.01% of chlorine. Therefore, RCl added into a raw mixture and are almost absent in clinker should not have had impact on synthesis of alite and strength properties of cement. However, results of physicommechanical tests of cements testify (Fig. 10) that when RCl is added the strength properties of cement is decreasing a little for 3 days and is increasing for 28 days.

To establish this dependence X-ray phase (Fig. 11) and the petrographic analyses of clinker (Fig. 12) were carried out. Roentgenograms of the clinkers burned at 1450°C, testify that RCl addition increases the reflections of calcium aluminoferrites (2.65 E) and decreases reflections of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  (2.69 E) probably as a result of  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3 + 3\text{CaO}\cdot\text{Al}_2\text{O}_3 \rightarrow 6\text{CaO}\cdot 2\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3 + \text{CaO}$  reaction. Extracted CaO raises the content of alite that is clearly seen on roentgenograms.

The petrographic analysis showed that RCl addition changes clinker microstructure increasing by ~10% small (< 15 microns) and for ~15% large (> 30 microns) crystals of alite. Perhaps, the reason of durability decrease of cement at an early stage of hardening is a small quantity of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ .

Further processes of hydration and hardening develop like hardening of mixed cement [13] which consists of two clinkers with small and large crystallization of alite. The small crystals create a large number of crystallization centers and the large ones provide their growth. The additional effect on the clinker activity is made by increasing content of  $3\text{CaO}\cdot\text{SiO}_2$ . It is peculiar feature of a clinker microstructure synthesized from slimes with additives of KCl and NaCl that increases durability of cement for 28 days.

According to differential thermal analysis the value of exothermal effect at 1300°C is less in mixtures with RCl, than in a mixture without additives. (Fig. 13) that testifies that a part of  $2\text{CaO}\cdot\text{SiO}_2$  was formed at lower temperatures. Therefore, the presence of small and large crystals  $3\text{CaO}\cdot\text{SiO}_2$  can be explained by the formation of alite from belit formed during various stages of burning.

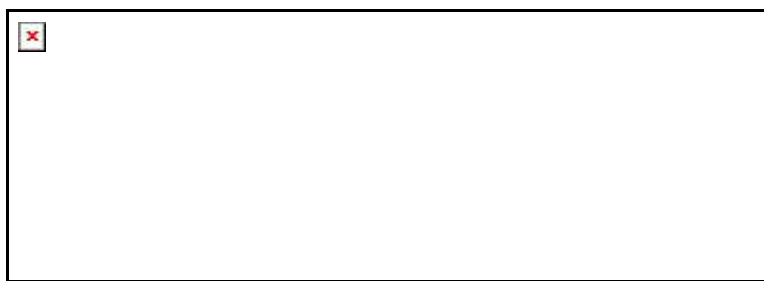


Fig. 13: The influence of RCl on the exo-effect of belite formation

## CONCLUSION

Ability of chlorides of alkalis almost completely to be sublimated, to make low-melting eutectics and to intensify formation of spurrite in the low-temperature area defines their greatest negative influence on technological processes of burning in the form of outgrowths and sows in comparison with sulfates. However, unlike carbonates and calcium and sodium sulfites, chlorides do not reduce quality of clinker. Therefore, to decrease circulation of alkali salts in the dry process of production it is recommended to output alkali containing dust by bypassing some amount of gases with their subsequent rational use.

**Conclusions:** The problem of impurities of salts of alkali metals in cement raw materials is their negative influence on technological processes of clinker burning and quality of cement owing to ability of these salts to evaporate in burning process and concentrate in oven system, forming outgrowths and sows. It is established that KCl and NaCl make the greatest impact on a nasty formation as they possess ability to excessive sublimation so the chlorine ion concentration in oven systems increases in 100 and more times and intensify the spurrite formation  $(2\text{CaO} \cdot \text{SiO}_2)_2 \cdot \text{CaCO}_3$  reinforcing deposits of salts.

- Before melting with the concentration increase to a particular limit chlorides intensify decomposition of  $\text{CaCO}_3$  destabilizing its lattice. The increasing amount of a melt sharply decreases the speed of dissociation process of  $\text{CaCO}_3$  because of the increase of fractional pressure of  $\text{CO}_2$  so there is need to overcome the surface intention of a film of the formed melt. Thus, melting in a mixture with  $\text{CaCO}_3$  begins before melting of pure KCl and NaCl as a result of formation of eutectics in binary systems of  $\text{CaCO}_3$  – RCl of structures 97.5 mole% of KCl and 2.5 mole

CaO% at 760°C and 97.1 mole% of NaCl and 2.9 mole CaO% at 792°C. It is possible the formation of eutectic in triple  $\text{CaCO}_3$ – CaO – RCl system melting point of which is 5–12°C below the above stated eutectics.

- Interaction of a clay component with KCl and NaCl is stated. It results from the effect of Hedvall due to changes in aluminosilicate lattice. Dehydration and influence of water vapor on decomposition of chlorides of alkali metals with  $\text{Cl}^-$  extraction is studied.  $\text{K}^+$  and  $\text{Na}^+$  ions combine with aluminosilicates.
- The differential scanning calorimetry combined with a mass spectrometry, established feature of sublimation of salts of alkali metals depending on an anionic component. So, negative influence of carbonates and sulfates of alkali metals on the quality of clinker is caused by their ability to sublime because they are present at all stages of synthesis of clinker and make immediate impact on clinker formation processes. The distinguishing feature of chlorides of alkali metals is practically their complete sublimation at the beginning of reactions of alite formation. To 1230°C large quantity chloride ion in patterns is less than 0.1% whereas in a raw mixture the content of  $\text{Cl}^-$  is 4%.

Therefore, when using the cement raw materials containing salts of alkali metals, especially chlorides even in quantity 0.01 percent to bypassing of furnace gases is recommended to prevent nasty formation.

- In raw mixture at the stage of dehydration of KCl and NaCl aluminosilicates accelerate interaction between  $\text{CaCO}_3$  and a clay component in raw mixture with spurrite formation  $(2\text{CaO} \cdot \text{SiO}_2)_2 \cdot \text{CaCO}_3$ . Intensifying effect of chlorides of alkali metals at early stages of mineral formation result in the formation of clinker

microstructure with high content of small and large crystals of alite formed from belit at various stages of burning and some decrease in tricalcium aluminate because of enrichment of calcium aluminoferrites by alumina that increases the content of tricalcium silicate.

## REFERENCES

1. Erhard, H.S. And A. Scheur, 1994. Brenntechnik und wärmewirtschaft. VDZ-kongress' 93: 278-295.
2. Locher, G. and H. Klein, 2009. Modeling circulating sulfur, chlorine and alkali systems in the clinker burning process; part 1: comparison of measurement and calculation. *International*, 3: 74-87.
3. Locher, G. and H. Klein, 2009. Modeling circulating sulfur, chlorine and alkali systems in the clinker burning process; part 2: theory and discussion. *Cement International*, 4: 64-75.
4. Enders, M. and U. Haeseli, 2011. Reactions of alkalis, chlorine and sulfur during clinker production. *Cement International*, 3: 38-53.
5. Tokheim, L.A., 2006. Kiln system modification for increased utilization of alternative fuels at Norcem Brevik. *Cement International*, 4: 52-59.
6. 169. Nobis, R., 2009. General report WDC Congress 2009: Burning Technology. *Cement International*, 5: 52-71.
7. 170. Klein, H. and V. Hoenig, 2006. Model calculations of the fuel energy requirement for the clinker burning process. *Cement International*, 3: 44-63.
8. Lopanov, A.N. and E.A. Fanina, 2012. Acid-base interactions of Sodium chloridum with calcium carbonate in the formation of cement clinker. *Cement and its Application*, 2: 90-93.
9. Kudin, L.S., G.G. Burdukovskaya and K.S. Krasnov, 1990. Mass-Spectrometric Study of Ionic Composition of Saturated Vapor of Potassium-Chloride. Formation Enthalpies of  $K_2^{+/-}$ ,  $K_3^{2+}$ ,  $KCl_2$  and  $K_2^{3+}$  Ions. *Zhurn.Fiz.Khim.*, 64(4): 909-914.
10. Shtark, Y. I. Harchenko, P. Krivenko, R. Runova, M. Kochevykh and I. Rudenko, 2001. Use of cement dust in slag binding systems. *Cement*, 9: 38-42.
11. Ivanov, N., 1997. Use of furnace dust. No. 8 of JSC Sebyakovtsement. *Structural materials*, 1: 23-27.
12. Schneider, C., M. Schulz and B. Hamman, 2007. Production of glass products – a possible new way of utilizing dusts from the cement industry *Cement International*, 1: 64-73.
13. Zhuravlyov, P.V., V.K. Klassen and A.N. Klassen, 2000. Synthesis of the low-sodium and low-power intensive clinker with the use of slags and production of high-quality mixed cement. *News of higher education institutions. Construction*, 10: 40-44.