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By-product materials in cement clinker manufacturing

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Abstract

The use of Cl- and SO_3-containing by-products from chemical industries for manufacturing Portland cement clinker using a wet process was examined. The chemical and mineralogical compositions of the by-products and raw materials were determined. Homogeneous raw mixes containing different concentrations of by-products (5–30%) were prepared and the influence of the by-products on all steps of burning the mixes in a kiln to form a cement clinker was investigated. It was shown that introducing Cl- and SO_3-containing by-products to the raw mixes significantly changes all the cement clinker producing stages and changes the chemical and mineralogical compositions at all intermediate stages and in the finished products, forming new minerals containing Cl and SO_3 [CaO_X $(SiO_2)_y$ $CaCl_2$] or [CaO_x $(SiO_2)_y$ $CaSO_4$] and increasing the amount of well-known intermediate minerals. The presence of the chlorides and sulfates in the cement clinker burning processes removes alkali from the raw mixes, turning them to volatile forms, accelerating the raw mineral decomposition processes and accelerating the formation processes of cement minerals (C_2S, $C_{12}A_7$, C_4AF) and formation of chloride and sulfate cycles in the kiln, forming clinker liquids and decreasing the formation and growth of the main cement minerals (C_3A, C_3S). The cement clinker contains some quantity of minerals with Cl or SO_3. Their presence in the final product decreases cement quality by reducing the amount of active CaO (C) and reducing the active CaO/SiO_2 ratio.

Keywords: Chloride; Sulfate; Alkalis; Clinker; Kinetics

In this paper we present results from the industrial testing of chlorine- and SO_3-containing by-products from chemical industries for manufacturing Portland cement clinker (Table 1). The chlorine-containing by-product is a semidry mix and results from industrial refinement of waste gases containing chlorine. The main components are calcium carbonate, calcium chloride, and alkali chlorides (KCl, NaCl). The concentrations of these components in the by-product may vary; therefore, the by-product must be homogenized (premixed) to be suitable for use. Another chlorine-containing by-product is an aqueous solution with the corresponding salts. The solution is almost saturated with calcium chloride (Table 1). The source of sulfate-containing by-product is chemical manufacture of phosphorous-containing fertilizers, where the phosphate-containing rock is treated with sulfuric acid. As a result of undergoing a reaction of substitution, gypsum or so-called phosphogypsum is formed.

These by-products contain calcium oxide or calcium carbonate and can be used as potential raw materials for manufacturing Portland cement clinker.

1. Experimental procedure

Before the industrial scale test, laboratory and pilot tests were performed [1–3], including all stages of raw mix preparation and burning of clinker, mineralogical compositions, hydration, and performance testing of the cements. These tests showed the possibility of using the by-products for manufacturing Portland cement clinker. The present tests were performed using wet process kilns with dimensions of 120 m × 4 m and 75 m × 2.5 m. Homogeneous raw mixes were prepared from ordinary limestone, argillaceous component, and sintered ferrites (pyrites).

2. Results and discussion

2.1. Chlorine-containing raw mixes

Investigation of the rheological properties of the slurries, which were prepared using chlorine-containing by-products, showed that the presence water-soluble chlorine salts ($CaCl_2$, NaCl, KCl) enabled the amount of water in the slurries to be reduced by up to 5% without changing their rheological properties. It also was found that the strength of the

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Table 1
Chemical composition of the raw materials and by-products (%)

	Water solution of $CaCl_2$	$CaCl_2$-containing by-product	Phosphogypsum	Limestone	Argillaceous comp.	Pyrite sinters
SiO_2	—	<1	8.38	2.78	51.24	9.09
Fe_2O_3	—	—	0.19	0.31	4.71	73.26
TiO_2	—	—	0.05	—	—	—
Al_2O_3	—	<1	0.75	0.45	12.18	1.55
CaO	—	39.00	29.06	53.59	12.08	4.11
MgO	—	<1	0.20	0.77	2.23	—
R_2O	—	—	0.30	0.06	2.88	—
SO_3	—	—	40.63	—	0.50	1.50
$CaCl_2$	40.00	17.00	—	—	—	—
RCl	10.00	8.00	—	—	—	—
P_2O_5	—	—	1.08	0.10	—	—
Loss	—	31.00	18.76	41.72	13.38	6.55
Others	50.00	2.00	0.60	0.22	0.81	3.94

dried raw slurries increased with increasing content of $CaCl_2$. The presence of alkali chlorides, however, had the opposite effect: they did not increase raw mix strength, rather they decreased it. But the resulting relative strength was higher than for raw mixes without chlorides (Fig. 1). Raw mixes containing 2%, 4%, and 6% chlorine were tested.

The kilns were equipped with chain systems, hatches, and dust filters. The firing procedures were the same as for firing conventional raw mixes. The chain systems dried and transported the raw mix toward the calcination zone. The earlier appearance (from 600°C) of liquids, based on the $CaCl_2$-KCl-NaCl salt system, which has low viscosity and high adhesion, contributed to the decomposition of the raw mix, raw minerals. The liquid created many fine particles. Alkali oxides, released after the decomposition of the raw minerals, reacted with $CaCl_2$ and formed RCl. The calcium oxide released and participated in the reaction of formation of clinker minerals. Calcium carbonate calcined earlier and faster, which contributed to the earlier formation of intermediate minerals. In the temperature range 1000–1200°C, all alkali chlorides evaporated (Fig. 2) from the firing mixes and were transported toward the chain system by the hot gases. In the colder areas of the kilns they partly precipitated on the surfaces and partly transported further to the dust catching area, where they accumulated with growing concentration. The RCl, which precipitated on the colder areas of the kilns, mixed with slurry, mud, and dry mixes and returned to the hot areas of the kilns. As result, it created a so-called alkali cycle, which included the calcination area and chain system. Sometimes rings were formed in, or upstream of, the calcination area. These rings disturbed the movement of the mix, making it irregular and undulating. At the same time the amount of dust the kilns is increasing, which makes it very difficult (sometimes impossible) to produce normal Portland cement clinker. All these problems are particularly significant when there are higher concentrations of $CaCl_2$ in the raw mixes. Intermediate and final cement clinker minerals do not contain alkali chlorides.

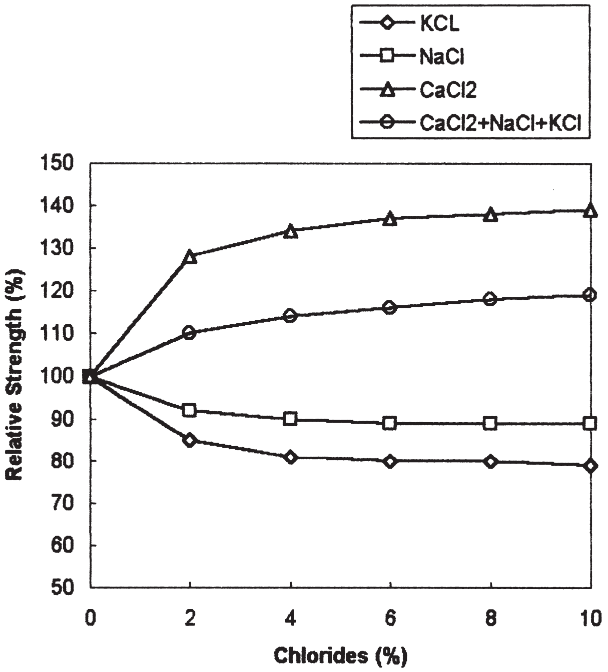

Fig. 1. Relative strength of the dry raw mixes containing chlorides.

Return of the alkali chloride-rich filter dust to the Portland cement clinker manufacturing process is not recommended. It would be desirable to find some means of using this collected dust to produce a useful product containing alkali chlorides.

The accumulation of alkali chlorides in the kilns and the formation of alkali and chlorine cycles contributes to the appearance of problems in the chain system associated with formation of slurry and mud rings. These problems are more significant for small kilns. Redesigning the chain systems may alleviate these problems.

The presence of $CaCl_2$ in the raw mixes contributes to earlier formation of intermediate minerals (C_2S, $C_{12}A_7$, $2C_2S \cdot CaCO_3$) and formation of new calcium-containing

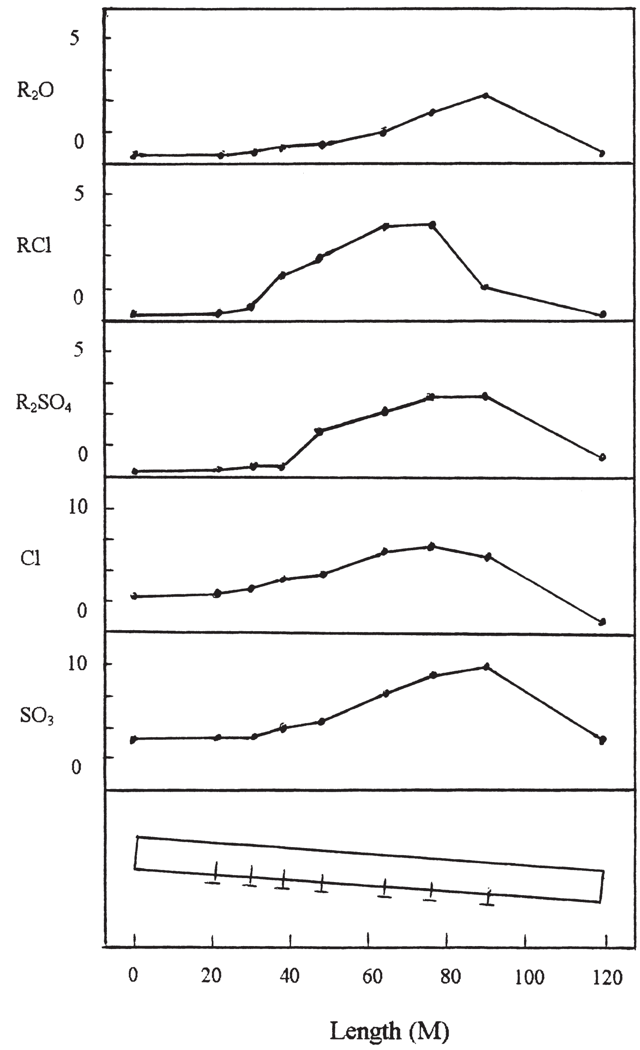

Fig. 2. Distribution of the alkali, chlorides, and sulfates (in %) along the kiln.

minerals ($C_{11}A_7 \cdot CaCl_2$, $2C_2S \cdot CaCl_2$). The $CaCl_2$ melt has a very good ability to readily dissolve oxides, particularly calcium oxide [2]. It has created a new kind of liquid (salt-oxide melt), which begins to appear at 700°C, when it is predominantly a salt melt, and changes to mostly an oxide melt when temperatures of 1200–1300°C and higher are reached. At about 1100–1200°C the intermediate mineral $2(C_2S) \cdot CaCl_2$ is decomposed, partly producing the regular C_2S and partly a new highly basic calcium chlorosilicate-alinite. Its chemical composition has been described as $Ca_{22}[Al_{0.25}Si_{0.75}]_8O_{36}Cl_2$ or $6(C_3S) \cdot C_3A \cdot CaCl_2$ [1]. Its content in the clinker can reach up to 50–70% (depending on the quantity of $CaCl_2$ in the raw mixes). At a temperature range from 1200–1300°C, the main Portland cement clinker mineral—alite—starts to form. Its content also depends on the presence of $CaCl_2$ in the raw mixes. When the amount of alinite is increasing, the amount of alite is decreasing. When the raw mixes contain 6% and more of $CaCl_2$, the clinker contains mostly the mineral alinite (pure mineral alinite contains 6.3% $CaCl_2$) [4]. Of course, the option of producing Portland cement clinkers containing a mixture of alite and alinite at variable proportions always is available [5,6]. Determination of the bulk quantity of defects by neutron activation, x-ray dispersion, and thermoluminescence analyses has shown that alinite-containing Portland cements have more lattice defects, which may enhance the cement's early strength development. For manufacturing regular, alite-containing, cement clinker, the firing time (or temperature) needs to be increased until complete decomposition of mineral alinite, decomposition of $CaCl_2$, evaporation of chlorine, and formation of the mineral alite takes place. It is significant that the decomposition of $CaCl_2$ in the absence of alkali oxides is a very complicated task. The presence of 4% or 6% of chlorine in the raw mix can have serious consequences. In the clinker nodulization zone, relatively low-viscosity chloride-rich melts are formed, which disrupt the normal nodulization process, creating rings, cakes, and big balls. These conditions make it impossible to use a relatively high quantity of $CaCl_2$ for manufacturing normal alite-rich Portland cement; it is only possible to produce a cement containing a mixture of alinite and alite "mixed" cement. The firing temperature is reduced to 1350–1400°C.

2.2. Phosphogypsum-containing raw mixes

Less than 1% sulfur oxide normally is present in the raw mixes used for manufacturing Portland cement clinkers. Significantly large amounts of SO_3 are used in special cements manufacturing technologies (expansive cements) [7–10]. There are sulfoaluminates, sulfosilicates, and sulfoferrites cements. These cements contain more than 10% SO_3 [11,12]. The main clinker minerals formed in these cements are $C_3A_3CaSO_4$-calcium sulfoaluminate, $2(C_2S) \cdot CaSO_4$-calcium sulfo-orthosilicate, and -C_2S- beta calcium orthosilicate. The main mineral of Portland cement clinker—alite—does not form in the SO_3-rich mixes. Our goal was to determine the quantity of phosphogypsum that can be used for producing ordinary Portland cement clinker.

Investigation of the processes of minerals formation demonstrate that in the $CaO\text{-}SiO_2\text{-}CaSO_4$ system [13–15], the solid solution between C_3S and $CaSO_4$ appears if the system contains more than 10% SO_3. The content of SO_3 in the solid solution phase may vary from 1% to 5.2% [14]. In the $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3\text{-}CaSO_4$ system [16,17], where the $CaSO_4$ content is up to 10%, alite (C_3S) is the most abundant phase. The main intermediate mineral is calcium sulfo-orthosilicate $2(C_2S) \cdot CaSO_4$, and the main aluminum oxide-containing mineral is a calcium sulfoaluminate $C_3A_3CaSO_4$. Utilization of more than 10% $CaSO_4$ while minimizing residual SO_3 in the clinker is no easy task. Decomposition of a large amount of gypsum and production of active calcium oxide requires much more time and energy.

Raw mixes with 4%, 7%, and 10% phosphogypsum were prepared to determine the technological feasibility of utilizing phosphogypsum and its desirable quantity in the raw mixes. The raw mixes were prepared from ordinary raw materials (Table 1). The firing procedure was the same as for normal raw mixes, assuming approximately 50% decomposition of gypsum. It was found that, during the firing process, alkali oxides, which were released after the decomposition of raw minerals, reacted with SO_3 and formed alkali sulfates. Gypsum and alkali sulfates melt and form a low-temperature eutectic melt. It is a primary liquid. It dissolves calcium, silicon, aluminum, and iron oxides and, after the temperature rises to 1300°C and above, dissolves intermediate sulfate-containing minerals. The properties of this liquid are different than those in normal Portland cement clinker [18], where it mostly consists of oxide: lower viscosity, a higher oxide diffusion rate, but with almost the same surface tension. At high temperatures, alkali sulfates, especially potassium sulfate, evaporated and were transported by hot gases to colder areas, where they partly precipitated on the colder surfaces and were partly transported to the dust catchment area (filters). The quantity of alkali sulfates, which are retained inside the kilns, are increased and create alkali and phosphate cycles. The potassium cycle is shorter and its concentration inside the kiln lower than that of sodium. In the filter dust the most abundant sulfate is potassium sulfate. Some of the sodium sulfate at times comes out with clinker after establishing an alkali cycle inside the kiln. The alkali sulfates are enriched in the filter dust, which cannot be returned to the kiln and may be used as a source of water-soluble alkali sulfates or in other applications requiring alkali sulfates.

Intermediate minerals are formed at the same time as raw minerals are decomposed. They are $2(C_2S)CaCO_3$, $2(C_2S)$-$CaSO_4$, and $C_3A_3CaSO_4$, followed by C_2S and C_4AF. The largest quantity of intermediate minerals is formed in the temperature range 1200–1300°C, when SO_3 is present in highest quantity. At higher temperatures the intermediate mineral $2(C_2S)CaSO_4$ is decomposed, releasing a large amount of C_2S. Almost all the aluminum oxide is present in the $C_3A_3CaSO_4$ mineral. The main clinker mineral alite starts to form at a temperature of 1350°C and above. Its content in the final product depends on the content of SO_3. When the content of SO_3 increases, the quantity of alite decreases. In the final product the intermediate mineral $2(C_2S)CaSO_4$ and an increasing quantity of calcium sulfoaluminate also are formed. The clinker, produced from a raw mix containing 10% of phosphogypsum for example, contained 4–6% free calcium sulfate. The total quantity of calcium sulfate in the clinker was about 6–9%. The firing procedure for this mix was not uniform. In the raw mineral decomposition area and alkali phosphate accumulation area, rings were formed. The thickness of the clinker coating in the burning zone also was increased. The clinker had a very broad size distribution with numerous cakes, balls, and lumps, which means that, in the nodulization area, there was an unusually high content of low-viscosity melt. Clinker manufactured from this raw mix contained an insufficient quantity of alite (20–30% instead of 50–60%).

3. Conclusion

Trials examining the feasibility of producing Portland cement clinker from mixes containing $CaCl_2$- and $CaSO_4$-rich by-product from the chemical industry makes it possible to draw some conclusions.

It is possibly to produce Portland cement clinker from raw mixes containing these by-products. The limiting condition for $CaCl_2$-containing by-product is the concentration of salts produced in the recycling load. The content of alkali chloride needs to be minimized and the content of calcium chloride maximized. By-products need to be premixed. The concentration of $CaCl_2$ in the raw mixes should not exceed 3–4%. The alkali chloride-rich filter dust, with concentrations of RCl up to 15–20%, cannot be returned back to the clinker manufacturing process. Utilization of this by-product should be considered separately.

The concentration of phosphogypsum in the raw mixes must correspond to 6–8% $CaSO_4$. Filter dust rich in alkali sulfates cannot be returned back to the kiln, to the Portland cement clinker manufacturing process, and alternative applications should be found. Another limitation is the concentration of SO_3 in the finished product—clinker. The concentration should be lower than 2–3%.

Thus, unfortunately, use of these by-products for manufacturing Portland cement clinker cannot solve all problems. There is a need for full-scale investigations to consider the requirements of the other industries. In the present paper we touched on some of pros and cons of utilizing these by-products for manufacturing Portland cement clinker.

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