Possibilities of Chromate Decreased Clinker

F.D. Tamás[2] L. Opoczky[1] , L. Sas[3]

[1]*Cement Research and Development Ltd. Budapest, Hungary*
[2]*University of Pannonia, Veszprém, Hungary*
[3]*Duna-Dráva Ltd., Vác, Hungary*

ABSTRACT

In the course of laboratory and and industrial investigations we have tested that reducing slag as well as of the setting of the sulfatization degree of raw meal. In clinker it is possible to to decrease the chromate content during manufacture and firing clinker. It has been tested that among fuel materials (petrol, natural gas or coal, etc.) *coal firing* is the best to produce reduced clinker of chromate content. This is capable to set the oxygen content of the kiln and the sulfatization degree of clinker.

1. Introduction

The chromate-reduced (max. 2 ppm [Cr(VI)] of soluble Cr-content) cement is usually done during the manufacture to mix reducing substance matter during milling or post-mixing; this means that the quantity of reducing substance is determined by the soluble [Cr(VI)]-content of the cement.

It is clear that the soluble [Cr(VI)] content is determined by the "total" Cr added by natural and alternative raw- and fuel-materials is determined at the manufacture of clinker.

In this research the following items are described: the oxygen level of the kiln, the sulfatization degree of raw meal or clinker as well as the added fuel are investigated, to decrease the soluble chromate content.

2. Experimental materials and methods

Materials were industrial as well as laboratory-made model clinkers. To clarify clinkers industrial tests and measurement were done.

The raw mixes (according to test parameters) were milled to approx. ~5000 cm^2/g specific surface (Blaine), homogenised and pressed into pellets. Pellets were fired in a lab kiln to 1460^oC in air (oxidizing) atmosphere for 30 mins. The fired model clinkers were investigated to free lime (by the ethylene-glycol method. To study to investigate of the burnability of clinkers Cr_2O_3 was added in several quantities (from 0,05 to 2,5 m/m) Cr_2O_3.

Additional wustite-(FeO)-containing slag was used to reduce the valence of Cr was used. To study the effect sulfatization degree the similar materials were used, with differing sulfatization degree (by admixing gypsum to the mixture). The total Cr-content was determined by the Hungarian standard MSZ 21978-18:1986, the soluble [Cr(VI)] was determined by an alternative method TRGS 613 (prEN 196-10:2005.

Model clinkers were investigated by XRD (JEOL JSM-35), by optical microscopy in reflected light and by electron microscopy (JEOL JSM-35) + microprobe (EDAX, LINK type). To study chromium according to clinker phases, several selective solutions were used (salycilic acid/metanol and sugar/distilled water) was used. The model clinkers were ground to ~ approx. 5000 cm^2/g specific surface (Blaine), adding gypsum approx. m/m% and investigated various physical and mechanical of these clinker.

2. Results

2.1 The effect of chromium (Cr) to the burnability of raw meal and clinker forming process

Our investigation proved that a part of trivalent chromium (Cr^{3+}) is converted to hexavalent chromium (Cr^{6+}), by the oxididing atmosphere of the kiln (Fig. 1.). The chromium is deteriorating the burnability of the raw meal, as it hinders tricalcium silicate (C_3S) The chromium content of clinker phases (m/m%): silicates (alite, belite) = 1.48, aluminate = <0.10, aluminoferrite = 0.60.

By investigating model clinkers the hexavalent chromium is converted to $(CrO_4)^{2-}$ as an anion-complex, primarily in the silicate phases (belite, alite). The SEM picture is showed in Fig. 2., jointly with the energy dispersive X-ray spectra. A part of hexavalent chromium is fixed as potassium chromate or dichromate in the clinker (K_2CrO_4 or $K_2Cr_2O_7$) (Fig. 3). By investigating industrial clinkers it comes that a low sulfatization degree increases water-soluble hexavalent chromium.

2.2 Reducing slag effect of [Cr(VI)] water-soluble chromium

It has been prepared two identical chemical/mineralogical composition, sulfatization degree and total chromium content, without reducing slag (K1) and with reducing slag (K2). The raw material composition, modules, , free lime content and total chromium content and [Cr(VI)]-content are shown in Table 1.

By the free lime content, both clinkers are of high burnability. It is clear that K2 clinker contains less water-soluble [Cr(VI)].

Same tests were made with industrial clinkers too (K3, without slag and K4, with slag). Their chromium content was: total chromium content: K3 = 152.0, K4 = 154.0, water-soluble chromium content [Cr(VI)], K3 =

16.6, K4 = 3.8. It is clear that the chromium content is similar, but the water-soluble [Cr(VI)] is much less (Table 2.).

By the microscopic investigation the (Fig. 4. K3 clinker is black, while K4 contains some light brown particles. This is an indication that the firing/sintering of slag-containing clinkers a local reducing effect takes place, and as a result, the [Cr(VI)] content is less.

The physical/mechanical effect is identical (Table 2.)

2.3 Effect of fuels of the water soluble [Cr(VI)]-chromium content

By measurements, experiments and observations the firing fuels are effective to reduce the soluble [Cr(VI)] content. As a proof a clinker was burnt from equal chemical/mineralogical content, equal fineness and equal chromium content by different fuels (by heavy oil fuel, natural gas, coal and coal + alternative fuel) and the water soluble [Cr(VI)] was investigated. Results are shown in Fig. 5. It can be stated that less water-soluble [Cr(VI)] is found in coal + alternative fuel fired clinkers.

The beneficial effect can be interpreted as the reducing atmosphere as well as the increase of sulfatization degree. Most positive effects are valid in the choice of alternative fuels, esp. if its particle size is more coarse than the coal.

3. Summary

The reduced chromate clinker (max. 2 ppm water soluble [Cr(VI)]-chromium) can be made in cement industry practice to intermix a reducing substance (either by the grinding of clinker or afterwards). It was found, by laboratory and industrial experimentation to produce this clinker during firing or manufacture of clinker.

It was proved that raw materials (natural or alternative) the Cr_2O_3 can be transformed to water-soluble [Cr(VI)], because of the oxidating atmosphere of firing. The quantity of [Cr(VI)] depends on the introduced Cr_2O_3 amount and the oxygen level of the kiln.

The burnabilty of raw meal is deteriorating by chromium and the formation of alite is hindered. In the oxydation atmosphere of the kiln the hexavalence chronium is mostly bound in the silicate phases (alite and belite) as a solid solution, sot it can be dissolved immediately – this is the cause that from the point of working safety this will not cause any problem.

The [Cr(VI)] however be bound as potassium chromate or –dichromate. Our investigation proved that equal Cr2O3 content the clinker contains less water soluble [Cr(VI)] if the sulfatization degree is lower. This is why by adjusting the sulfatization degree less water soluble chromium remains in the clinker.

Our investigations proved that an admixture of reducing (FeO-containing) slag the water-soluble Cr^{6+} admixture can be decreased.

During the firing/ sintering of clinker in the vicinity of chromium containing particle a local reducing atmosphere is produced; this means either that it remains in trivalent state, or the previously oxidised Cr^{6+} is reduced into Cr^{3+}. In order to suitable reducing – besides the quality and quantity of reducing agent – also the fineness and complete admixing is a important factor.

Another factor is important to the quantity of water soluble [Cr(VI)] content: the fuel used to firing. Our investigations (both laboratori and industrial) proved that *coal-firing* is the best. This fuel is decreasing the oxygen level in the kiln and increasing the sulfatization degree: both factors decrease the water-soluble [Cr(VI)] content of clinker.

It is obvious to produce chromate-reduced cement is to add reducing substance to clinker or cement. However when manufacturing this cement it is important to add a substance during clinker manufacture, although these are from technological and clinker quality problems difficult. To produce this cement it is important to use both methods.

References

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[2] Sas, L. – Szabo, L. – Müller, A.: The effect of sulfatization degree of crystal structure and reaction ability of tricalcium aluminate. Epitoanyag *53* pp. 48-52 (2001) (In Hungarian)

Figures.

Fig. 1. C_3S and C_2S content with various amounts of Cr_2O_3

Fig. 2. SEM micrograph and energy dispersive X-ray spectra of clinker containing 0.1 m/mCr_2O_3

Fig. 3. Sodium chromate in clinker of low sulfatization degree

Fig. 4. Texture of K3 and K4 (with and without slag)

Fig. 5. Fuel effect on the water-soluble [Cr(VI] chromium content (in % of total chromium content)

Tables

Table 1.

Model clinkers with and without reducing slag

		K1	**K2**
Raw mixture (m/m%)	limestone	70,94	63,72
	clay	25,72	25,72
	pyrite cinders	3,44	nil
	reducing slag	nil	12,13
Moduli	KST	93,0	93,0
	SM	1,7	1,7
	AM	1,05	1,05
Properties of clinker	free lime	173,0	173,0
	total Cr (ppm)	173,5	173,0
	soluble [Cr(VI)] (ppm)	22,3	13,0

Table 2.

Physical/mechanical properties of industrial clinkers

Number of clinker	Total chromium (ppm)	Water soluble [Cr(VI)] (ppm)
K3	152,0	16,6
K4	154,0	3,6

Figures

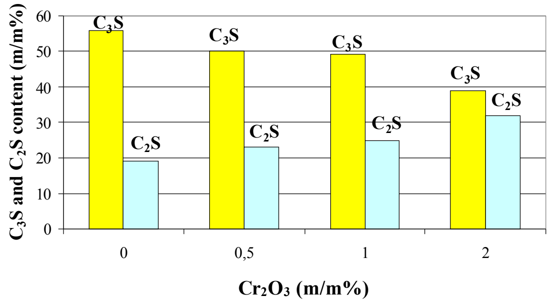


Figure 1. C_3S and C_2S content of clinkers with various amounts of Cr_2O_3 [1]

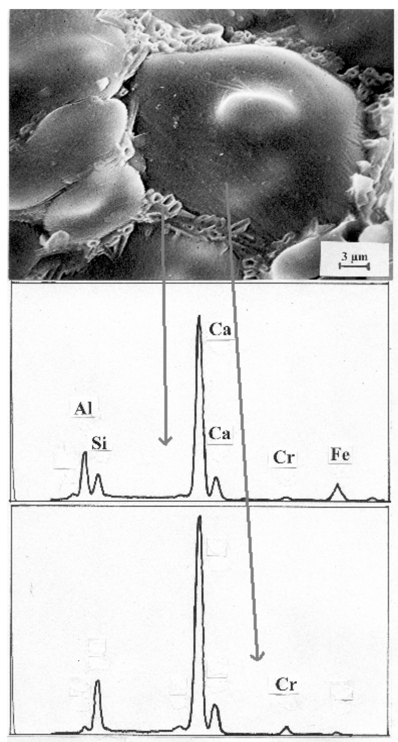


Figure 2.

SEM micrograph and energy dispersive X-ray spectra of clinker containing 0.1 m/m% Cr_2O_3

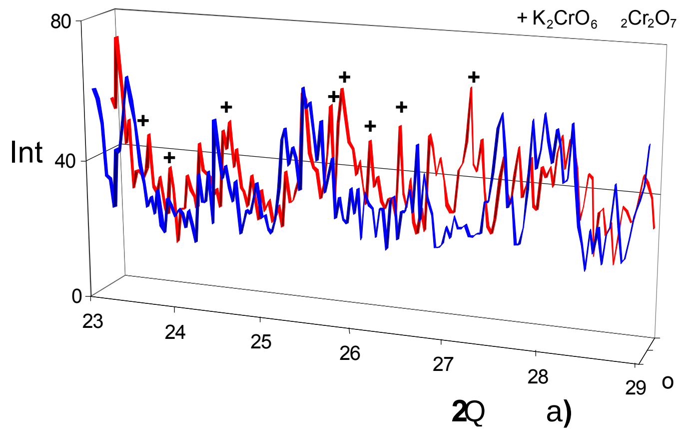
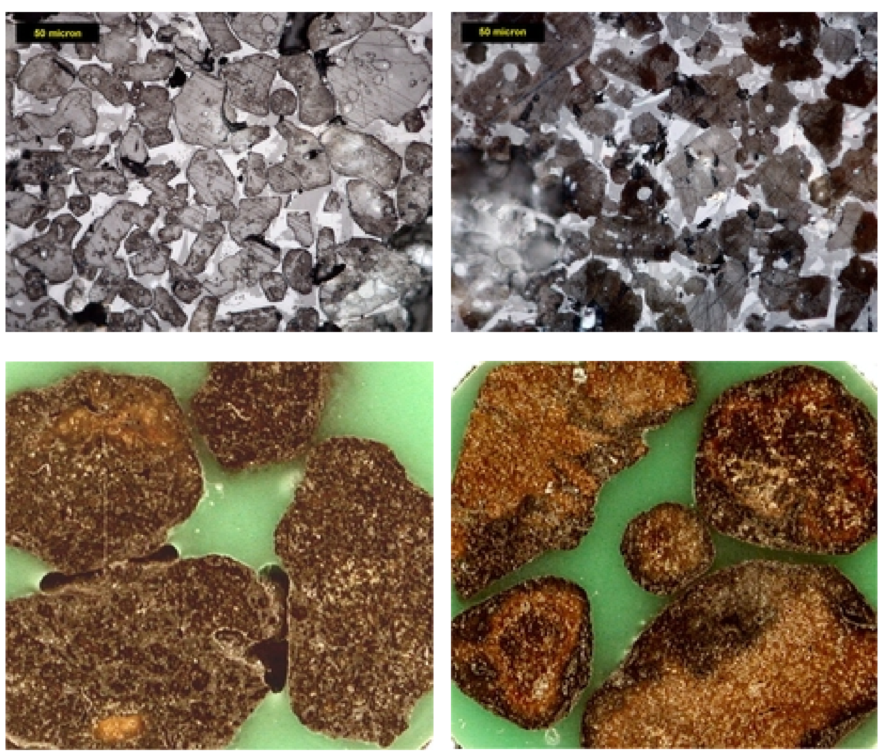


Figure 3.

Potassium chromate in high solubility [Cr(VI)]-chromium containing in clinker (low sulfatization degree)

K$_{\mathbf{etalon}}$ **K**$_{\mathbf{experimental}}$



Picture 4. Reducing slag effect of clinker texture

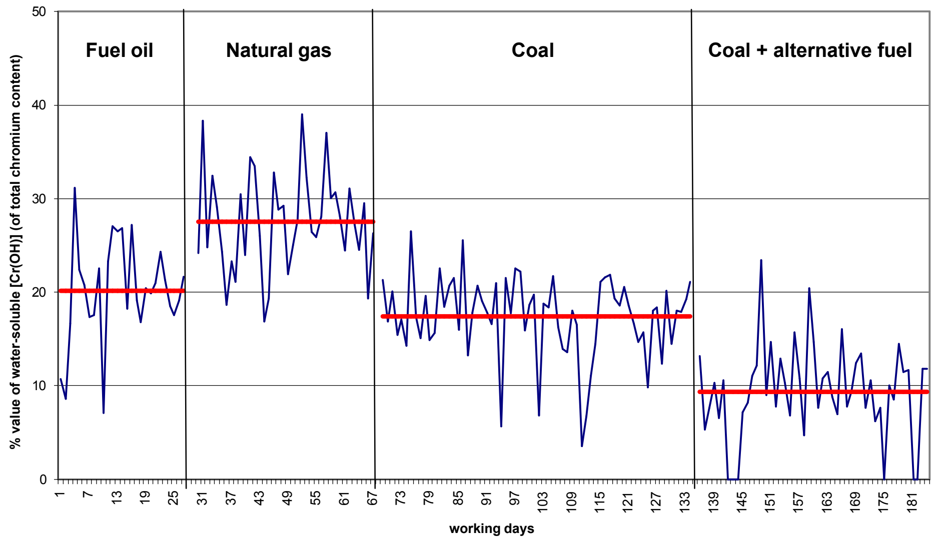


Figure 5.

Fuel effect on the water-soluble [Cr(VI)] chromium content

(in % of total chromium content)