15th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2011, Prague, Czech Republic, 12-18 September 2011

EFFECT OF RAW MATERIALS AND REDUCTION AGENTS ON HEXAVALENT CHROMIUM LEVELS IN PORTLAND CEMENT

Ilvana Tanjić, Amira Cipurković, Snežana Mičević
Department of Chemistry, Faculty of Science, University of Tuzla, Tuzla
Bosnia and Herzegovina

Vahida Selimbašić
Department of Environmental Protection, Faculty of Technology, University of Tuzla, Tuzla
Bosnia and Herzegovina

Eldin Halilčević
Faculty of Mininig, Geology and Civil Engineering, University of Tuzla, Tuzla
Bosnia and Herzegovina

Mugdin Imamović
Fabrika cementa Lukavac, Lukavac
Bosnia and Herzegovina

ABSTRACT
Raw materials for Portland Cement manufacturing in Lukavac contain chromium in trace quantities. In the oxidizing and alkaline burning conditions of the cement kiln, some of this is oxidized to Cr^{VI}. As a result, clinkers and cements contain soluble chromates, which are toxic and cause skin irritation and allergic enzema among workers. The European Community Obligation (Directive 2003/5C/EC) for soluble chromates level is bellow 2 ppm. Chromium(VI) levels in cement produced is Lukavac is up to 8 ppm, with the majority between 5 and 7 ppm. Chromate has high oxidizing effectiveness, because of its high ambition to switch over to the level of the trivalent Cr by addition of oxidizable substances as ferrous sulfate, stannous sulfate or antimony(III) compounds. When these reducing agents are added in sufficient quantity, they prevent the chromium from dissolving in watter removing the risk of dermatitis. In this paper, the effect of $FeSO_4 \cdot 7H_2O$ and H_3SbO_3 on Cr^{VI} reduction is compared by measuring Cr^{VI} content before and after adding of reducing agent in cement samples (standard method EN 196-10).
Keywords: cement,clinker, chromate, ferrous sulfate, antimony(III) compound

1. CHROMIUM IN CEMENT
Raw materials for manufacture of Portland cement in Lukavac contain traces of chromium.Chromium in the cement can originate from: 1) raw materials or fuel, 2) magnesia-chrome kiln refractory brick, if used, 3) wear metal from raw mill grinding process, if chromium alloys are used, and 4) additions such as gypsum, pozzolans, ground granulated blast furnace slag, mineral components, and cement kiln

dust. Total chromium from primary raw materials and finished products in the Factory of Cement Lukavac (FCL) depends on the type and origin, and its values are given in Table 1.

Table 1. The concentration of chromium (ppm) in raw materials and coal used in cement manufacturing in the FCL

Raw materials	Concentration (ppm)	Raw materials	Concentration (ppm)
Limestone	0,282	Slag	0,134
Ash	1,994	Gypsum	0,002
Sand	1,520	Coal	0,994

The cement process, specifically kiln conditions, can influence how much Cr (VI) will form. In the kiln, oxidizing atmosphere will play the largest role, with more oxygen in the burning zone leading to increased Cr (VI) formation. Alkali concentration is also of importance, since Cr (VI) in clinker is primarily in the form of chromates. In the finish mill, thermodynamically favorable conditions for oxidation to Cr (VI) exists, including high air sweep, moisture from gypsum dehydration, cooling water injection, and grinding aids, along with the high pH of the cement.[1]

As a result, clinkers and cements contain soluble chromates, which are toxic and cause skin irritation and allergic enzema among workers. *T*ouching wet cement with bare hands may cause skin problems. First of all, an irritant dermatitis caused by the alkaline nature of cement mixed with water. The result is a rash that disappears after a few hours. Secondly, an allergic dermatitis caused by water soluble hexavalent chromium Cr (VI) naturally present in most cements. When dissolved hexavalent chromium penetrates the unprotected skin and, inside the body, it is transformed into trivalent chromium, a molecule which combines with epidermal proteins to form the allergen that causes sensitivity to certain persons. This allergic problem only occurs in certain individuals who are particularly sensitive and it is permanent. [2] Besides exposing lame can lead to perforation of the nasal septum. Ulcers and perforation of the nasal septum caused by chromium is usually seen in workers in the industry, and can also occur without any side effects allergy to chromium.

The use of materials to reduce the level of Cr (VI) formation is especially prevalent in the European cement industry due to the 2003 European Directive which prohibits sale of cement containing more than 2 ppm of soluble Cr (VI) when hydrated. This has a significant economic impact on the cement industry. The concentrations of hexavalent chromium in the samples of cement produced in Lukavac mostly ranging between 5 and 7 ppm, a maximum of 8 ppm.

The characteristic of chromates is its high oxidizing effectiveness, because the chromates have a high ambition to svvitch over to the level of the trivalent chromium by addition of oxidizable substances[3]:

$$CrO_4^{2-} + 8\ H^+ + 3\ e^- \rightarrow Cr^{3+} + 4\ H_2O \quad (1)$$

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O \quad (2)$$

Addition of reducing reagents, such as iron(II) sulphate or antimony(III) compounds, in sufficient quantity, prevents the dissolution of chromium in the water and removes the risk of dermatitis.

2. THE REDUCTION OF SOLUBLE CHROMATES

2.1. The reduction of soluble chromates with $FeSO_4 \cdot 7H_2O$

While Cr(VI) is a strong oxidizing agent in acid solution, in an alkaline media (such as the cement mixing water) the situation is completely different and it is impossible to reduce the Cr(VI) with most of the reducing agents which usually work at a pH lower than 7. The reason lies in the fact that the redox potential of the couple Cr(VI)/Cr(III) changes with pH. Using the Nernst equation it is possible to calculate the value of redox potential at different pH and evaluate, from a thermodynamic point of view, which redox pair can reduce Cr(VI) to Cr(III). [4] The reduction of soluble chromates is usually obtained with the addition of ferrous salts during cement grinding. Natural heptahydrate is found as an alteration product of iron sulfides as the mineral melanterite, or can be an industrial by-product. It is soluble in water, its aqueous solutions are oxidized slowly by air when cold and rapidly when hot, and the oxidation rate is increased under alkaline conditions. Addition rate is usually 0.5% by mass. [5]

Iron form poorly soluble hydroxides in alkaline media, and this lowers the redox potential of the pair Fe(III)/Fe(II), allowing the reduction of Cr(VI) u Cr(III) according to the following equation [6]:

$$CrO_4^{2-} + 3Fe(OH)_2 + 4H_2O \rightarrow Cr(OH)_3 + 3Fe(OH)_3 + 2OH^- \quad (3)$$

The mechanism of action of ferrous salts can be considered as follows:

- as soon as the cement (ground with the reducing agent) is mixed with water, chromates and ferrous salts are released in solution, while the pH quickly increases following the hydration of cement;
- Fe^{2+} ions form insoluble hydroxides, their redox potential drop (in particular as the pH increases, their redox potential drop faster than the redox potential of Cr^{6+}) and the $Fe(OH)_2$ become strong reducing agent;
- Soluble chromates are reduced to $Cr(OH)_3$.

2.2. The reduction of soluble chromates with H_3SbO_3

The efficacy and the superior performances of this reducing agent is based on the redox properties of antimony(III). The pair Sb(V)/Sb(III) has a redox potential in alkaline solution E = - 0.59 volt [2]. From a thermodynamic point of view, this means that Sb(III) is a strong reducing agent at highpH and can reduce Cr(VI) present in the cement mixing water, according to the following equation [1]:

$$2CrO_4^{2-} + 3H_2SbO_3^- + 2H_2O \rightarrow 2Cr(OH)_3 + 3SbO_3^- + 4OH^- \quad (4)$$

In comparison to ferrous salts, Sb(III) compounds have weaker acid properties. This is an interesting advantage, because the reaction with free lime does not proceed, avoiding any loss of effectiveness during cement grinding or storage, even in the case of high free lime content and high level of humidity. As a result, the reduction performance of antimony(III) is unaffected by moisture and high grinding or storing temperatures. The reducing properties of antimony(III) remain unchanged even after more than one year.

3. RESULTS

The paper compared the effect of $FeSO_4 \cdot 7H_2O$ and H_3SbO_3 on the reduction of Cr(VI) by measurement of Cr(VI) before and after adding the reducing agent in cement samples (the standard method EN 196-10). Immediately before analysis, prepared samples were taken in accordance with EN 196-7, to obtain homogeneous samples. The samples were mixed well making sure the contact cement and the surrounding air is as short as possible. Cement is mixed with reagent for reduction and water at a precisely defined ratio and time, and thereafter filtered. The sample filtrate is treated with s-diphenyl carbazide and acidifies to low pH. Chromium(VI) in acidic solution forms a red-violet complex whose absorption is measured on a spectrophotometer at 540 nm. [7] The concentration of water soluble Cr(VI) is read from the calibration curve. The results obtained after the action of reducing agents H_3SbO_3 and $FeSO_4 \cdot 7H_2O$, and the reduction of hexavalent chromium are shown in Table 2. The results obtained are graphically shown in Figures 1 and 2.

Table 2. Results in the reduction of hexavalent chromium action $FeSO_4 \cdot 7H_2O$ and H_3SbO_3

No.	Additive		Cr^{6+} content in cement (ppm)		
	Reducing agents	Dosage (%)	Before additive	After additive	Degree of Cr(VI) reduction (%)
1	H_3SbO_3	0,02	7,96	2,2	72,4
2	H_3SbO_3	0,04	7,10	0,0	100
3	H_3SbO_3	0,04	6,95	0,1	98,6
4	H_3SbO_3	0,04	8,05	0,1	98,8
5	$FeSO_4 \cdot 7H_2O$	2,0	5,18	0,21	96
6	$FeSO_4 \cdot 7H_2O$	2,0	6,10	0,25	96
7	$FeSO_4 \cdot 7H_2O$	2,0	5,10	0,19	96,3
8	$FeSO_4 \cdot 7H_2O$	1,8	5,30	0,27	95

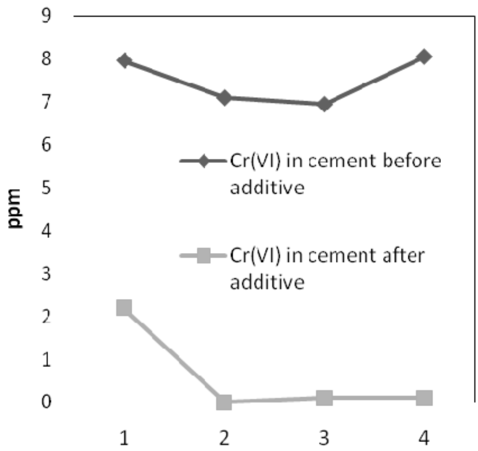

Figure 1. Reduction Cr(VI) with H_3SbO_3

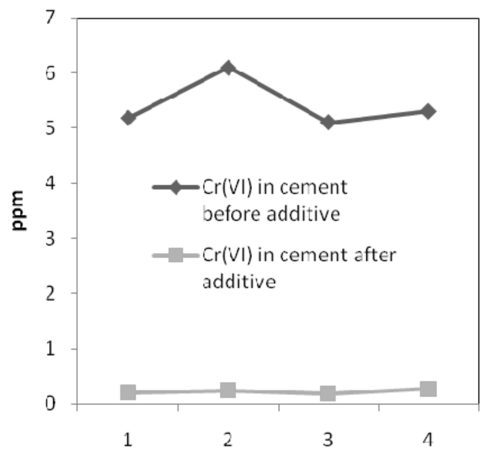

Figure 2. Reduction Cr(VI) with $FeSO_4 \cdot 7H_2O$

4. CONCLUSIONS

The use of antimony(III) compounds for the reduction of hexavalent chromium in cement and cement based materials presents interesting advantages in relation to the application of iron (II) salts:

- Ferrous sulphate presents serious problems related to the durability of the reducing properties: it is very sensitive to moisture and temperature and tends to loose effectiveness after grinding and during cement storage. This requires the use of very high dosages of ferrous sulphate, with costs higher than expected and undesired effects may occur.
- Due to the high stability and low acidity of antimony(III), these reducing agents are insensitive to temperature and humidity and are not affected by the presence of high levels of free lime. This allows superior performances to be obtained in comparison to the usual reducing agents based on ferrous salts.

5. REFERENCES

[1] Hills, L., C. Johansen, V.:Hexavalent Chromium in Cement Manufacturing: Literature review, Portland Cement Association (2007), R&D Serial No.2983.,
[2] Avnstorp, C.: Risk factors for cement eczema. Contact Dermatitis 25, 81-88, 1991.,
[3] Brandt, B., Bonder, W.: Reduction of chromates in hydraulical binders and the CEM-PROTECTOR® - SYSTEM, Scientifical informtion, Edition/Issue: October 2006/3.,
[4] Magistri, M., Padovani, D.: Chromates reducing agents, International Cement Review, 10-2005.,
[5] Hills, L., C. Johansen, V.:Hexavalent Chromium in Cement Manufacturing: Literature review, Portland Cement Association (2007), R&D Serial No.2983.,
[6] Magistri, M., D`Arcangelo, P.: New chromium reducing agent for cement, ZKG INTERNATIONAL, 61 (2008), No. 3. pp. 53-59.,
[7] Uputstvo za određivanje Cr^{6+} (EN 196-10).