DOI: 10.7251/JEPM1204007M
UDK: 631.4
Scientific paper

PEROXIDE TREATMENT IN EFFLORESCENCE PREVENTING

Jozefita Marku[1], Kozeta Vaso[1]
markujoz@yahoo.com

[1]*University of Tirana, Faculty of Natural Sciences, 1001 Tirana, Albania*

Abstract

Efflorescence is a crystalline deposit of water soluble salts on the surface of ceramic masonry. In most cases, efflorescence can be removed by various cleaning methods depending on the chemistry of the crystalline deposit. But this, sometimes, may even worse the problem.

Therefore, it would be most desirable to minimize or to prevent the efflorescence through the proper selection of raw materials and by addition of appropriate admixtures and supplementary materials.

Using clay with a high content of soluble salts, the aim of this experimental work was to evaluate the effect of H_2O_2 *addition in efflorescence minimization. Some experiments are done using various concentrations of aqueous solutions of hydrogen peroxide. The oxidizing solutions are added to clay during various mixing times, prior to the forming stage.*

The content of the soluble salts in the fired clay specimens is evaluated qualitatively and quantitatively.

***Key words**: peroxide, efflorescence, crystalline deposit, forming stage*

INTRODUCTION

Efflorescence is an aesthetic nuisance in the masonry industry that comes in many forms and is due to numerous causes.

Three conditions must exist before efflorescence occurs. Firstly, there must be water soluble salts present somewhere in the wall.

Secondly, there must be sufficient moisture in the masonry to render the salts into a soluble solution. Thirdly, there must be a path for the soluble salts to migrate through the surface where the moisture can evaporate, deposit the salts and then crystallize. If any of these conditions is not present, efflorescence can not occur [1].

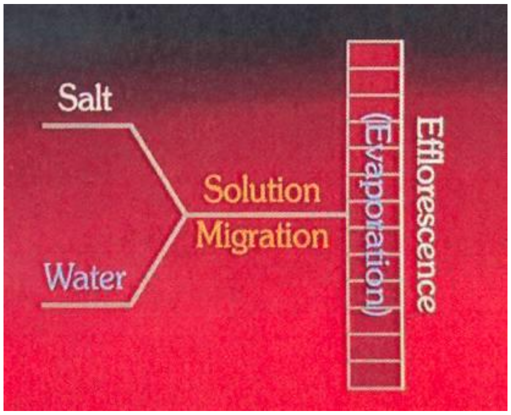

Figure 1. Three conditions of efflorescence occurrence

Figure 2. Typical white efflorescent salts on masonry

Therefore, to prevent efflorescence, the goal is the minimization of one or more of the conditions. Water-soluble salts present in only a few tenth of one percent are sufficient to cause efflorescence on a masonry surface. The amount of salts and character of the deposits can vary widely, according to the nature of the soluble materials and atmospheric conditions.

Efflorescence producing salts are usually sulphates of sodium, of potassium, of magnesium, of calcium, and occasionally of iron and/or carbonates of sodium, of potassium, and of calcium. There are a number of potential sources of soluble salts that could contribute to appearance of efflorescence on ceramic products during service even though the product itself is free of the soluble salts. Such sources may be: raw materials, de-icing materials, bedding materials, sand and cement in mortar, fertilizers, ground water, cleaners, etc [2].

The diagram shown below provides a good summary of the chemical contributors to the efflorescence.

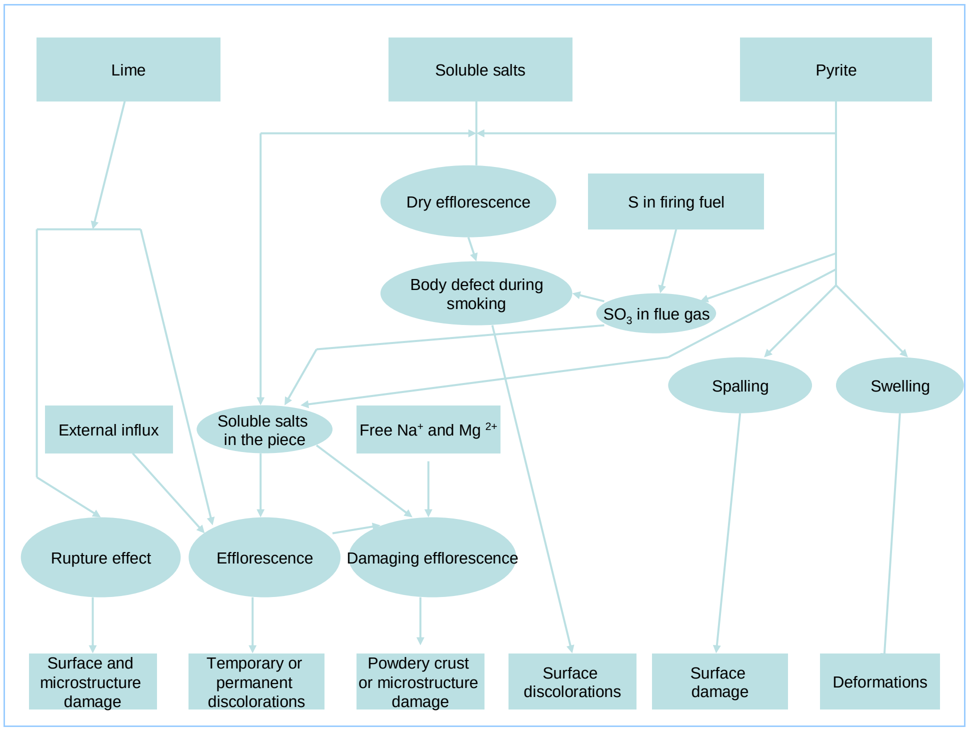

Figure 3. Material contributors to efflorescence

It is very difficult to totally control any one of three conditions of efflorescence occurring, but it is relatively simple to reduce the effect each one has towards efflorescence.

Despite all efforts, efflorescence may occur many times. Cleaning efflorescence from masonry walls does not cure the problem, it only removes the symptoms. After cleaning, the efflorescence will reappear unless the natural efflorescence chain has broken.

The best way of efflorescence minimization is the proper selection of clay raw materials and the addition of appropriate admixtures and supplementary materials [5].

EXPERIMENTAL PART

This study is focused on the occurrence of the negative phenomenon of efflorescence in ceramic bricks produced in the Ceramic Brick Factory in Lushnja, Albania.

The clay used has a high content of soluble salts, so the efflorescence deposits are common on the fired bricks produced in this factory. To evaluate the efflorescence minimization, supplementary materials such as $BaCO_3$, and H_2O_2 solutions are added to the clay raw material.

The addition of $BaCO_3$ in the clay during the grinding step, converts the soluble sulphates present in the clay, into insoluble form of $BaSO_4$, according to the reaction:

$$Na_2SO_4 + BaCO_3 = Na_2CO_3 + BaSO_4$$

After grinding, the clay raw materials containing pyrite may be mixed with an oxidizer such as H_2O_2 in a pre-oxidation step in order to disperse the oxidizer within the clay and to expose the maximum amount of surface of clay grains to the oxidizer. So, the prior removal of SO_2 and the subsequent one during firing at elevated temperatures may assist in preventing efflorescence caused by sulphur-containing compounds during firing of the products.

The oxidation of pyrite occurs in two steps:

$$FeS_2 + O_2 \rightarrow FeS + SO_2$$

$$2FeS + 7/2O_2 \rightarrow Fe_2O_3 + 2SO_2$$

Other oxidizing agents that may be employed to oxidize pyrite include: barium nitrate, potassium nitrate, sodium nitrate, potassium chlorate, ammonium perchlorate, magnesium perchlorate, calcium hypochlorite, sodium chlorite, barium peroxide, sodium peroxide, sodium percarbonate, lithium aluminium hydride, ozone, etc [3], [4].

In the first part of our study is evaluated the efflorescence deposit occurrence in fired ceramic products, produced with clay without any additive.

The chemical composition of studied clay and the chemical content of its aqueous extract are shown in the Table below:

Table 1. The chemical composition of Lushnja clay and its aqueous extract

Oxides (in %)	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**H/K**	**SO_4^{2-}**	**Cl^-**	**Dry residue in 180°C**
Clay of Lushnja	45.84	11.13	7.05	9.73	5.91	14.56	1.03	-	-
Aqueous extract of clay	-	-	-	-	-	-	0.112	0.11	0.324

The plasticity of clay was 11 Atteberg. According to appropriate standards, the plasticity of clays used in traditional ceramic production, varies within the interval of 10-20 Atteberg.

So, in our experiments, no supplementary material is used as additive to enhance or to reduce the clay plasticity.

The normal water content to form normal ceramic paste was 29%. Some small bricks are formed in moulds (4x4x16 cm) with clay without any additive. The green bricks are dried for 4 hours at 60°C and subsequently are fired for 4 hours in muffle furnace, at 950°C. The total shrinkage after firing was 7.8% (drying shrinkage 6.4% and firing shrinkage 1.4%).

The chemical analyses of studied clay showed that the content of sulphate and chlorure ions, as well as the total quantity of soluble salts was high. The content of iron was high, too. Water soluble sulphates (especially those with high content of crystalline water), cause the efflorescence of fired products, even when are present at least 0.01% SO_4^{2-} (of dry clay).

Sulphates that are hardly soluble in water cause efflorescence when they are present above 0.05% SO_4^{2-}. Whereas the iron is linked to “sulphur efflorescence” when is present in clay as pyrite or as sulphide.

So, the efflorescence deposit was evident at the fired ceramic bricks produced without any ameliorative additive.

Figure 4. The efflorescence white deposits occurred on fired prisms made with clay without ameliorative additive

In this study is evaluated the efflorescence occurrence caused only from the salts present naturally in clay raw material and not that caused by soluble salts accumulated in products during the drying and firing process. The formed products are dried and fired in laboratory dryer and muffle furnace. But dryers used in traditional ceramic production are typically fed by waste heat drawn from the cooling zone of the kiln. It is clear that, practically, in those conditions the efflorescence occurrence would have been more intensive because of the additional presence of SO_2 of the fume gases.

In the second part of the study is evaluated the influence of supplementary materials in efflorescence deposit occurrence minimisation. As supplementary materials are used $BaCO_3$ and H_2O_2 solutions 1 and 3%. $BaCO_3$, at different quantities, is mixed with clay which was dried at 105°C and sieved to eliminate grains over 1mm. H_2O_2 solutions at different concentrations are sprayed into the clay.

The method used consisted of the use of oxidizing solution prior to heating of the clay. It includes the mixing of the clay with the oxidizing solution, dispersing it within the clay, pre-oxidizing the pyrite and then shaping the clay into products and then firing which further oxidizes the pyrite. The mixing time of 1 hour and 2 hours are used. Thirteen paste mixes are made with incorporation of $BaCO_3$ and solution of 1 and 3% H_2O_2.

Table 2. The ingredients of paste mixes prepared with clay and supplementary additives $BaCO_3$ and H_2O_2 solutions

The ingredients of recipes (%)	**A_1**	**B_1**	**B_2**	**B_3**	**B_4**	**B_5**	**H_1**	**H_2**	**H_3**	**H_4**	**H_5**	**H_6**	**H_7**	**H_8**
Clay	100	100	100	100	100	100	100	100	100	100	100	100	100	100
$BaCO_3$	–	0.075	0.112	0.225 (stechiom)	0.45	0.56	–	–	–	–	–	–	–	–
H_2O_2 (solution 1%)	–	–	–	–	–	–	14.5	7.3	-	-	14.5	7.3	-	-
H_2O_2 (solution 3%)	–	–	–	–	–	–	–	–	14.5	7.3	–	–	14.5	7.3
Forming water	29	29	29	29	29	29	14.5	21.7	14.5	21.7	14.5	21.7	14.5	21.7
H_2O_2 solution: forming water ratio	-	-	-	-	-	-	1:1	0.5: 1.5	1:1	0.5: 1.5	1:1	0.5: 1.5	1:1	0.5: 1.5
Mixing time (min) before shaping	5	5	5	5	5	5	60	60	60	60	120	120	120	120

With each of paste mixes, three prisms are formed in moulds of 4x4x16 cm. They are dried and fired at the same conditions as the prisms formed with clay without additive.

To identify the presence of efflorescence deposits three methods are used. Aqueous extract of green pastes (Qualitative test I): A quantity of 50 g of green paste from each recipe is mixed with 500 ml distilled water. After 24 hours the suspension is filtered. The filtrates are examined for the presence of barium sulphate by adding of barium chloride. Identifying the efflorescence deposit (Qualitative test II): The fired prisms are dipped in distilled water in 1/3 of their height for 48 hours and then are examined visually for efflorescence deposit. Aqueous extract of fired pastes (Quantitative test): These analyses are done according to the European Standard EN 771-1. A quantity of 250 g from each fired prism is ground and sieved. 20 g powder (passing 150 µm sieve) is mixed with 700 ml distilled water for 1 hour. The extracts are analyzed for the quantity of chloride, sulphate, sodium, potassium ions, and dry residue in 180^oC.

RESULTS

The results of efflorescence identification tests are shown in the Figures below:

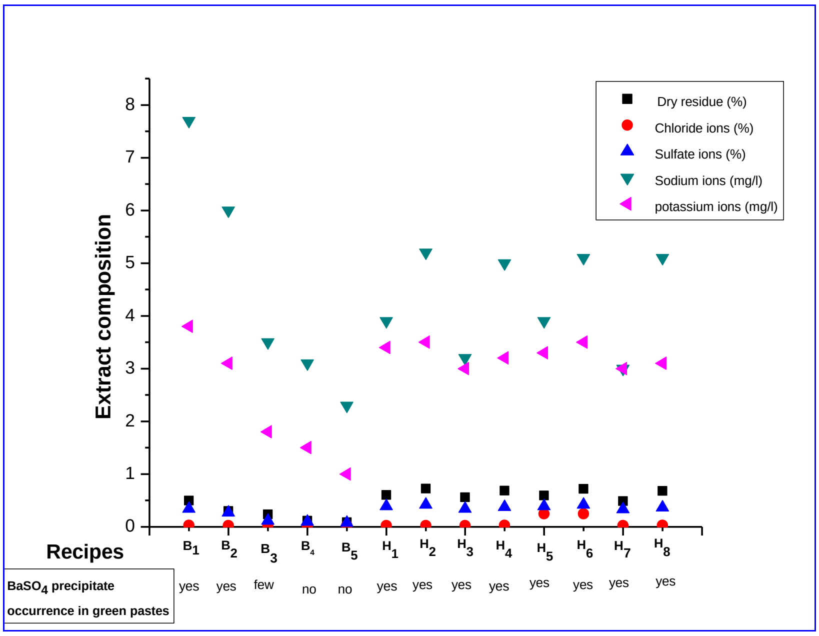

Figure 5. The results of visual examination of aqueous extracts of green paste mixes (Efflorescence Qualitative test I, below) and the results of analyses of aqueous extracts of fired ceramics (Efflorescence Quantitative test, above)

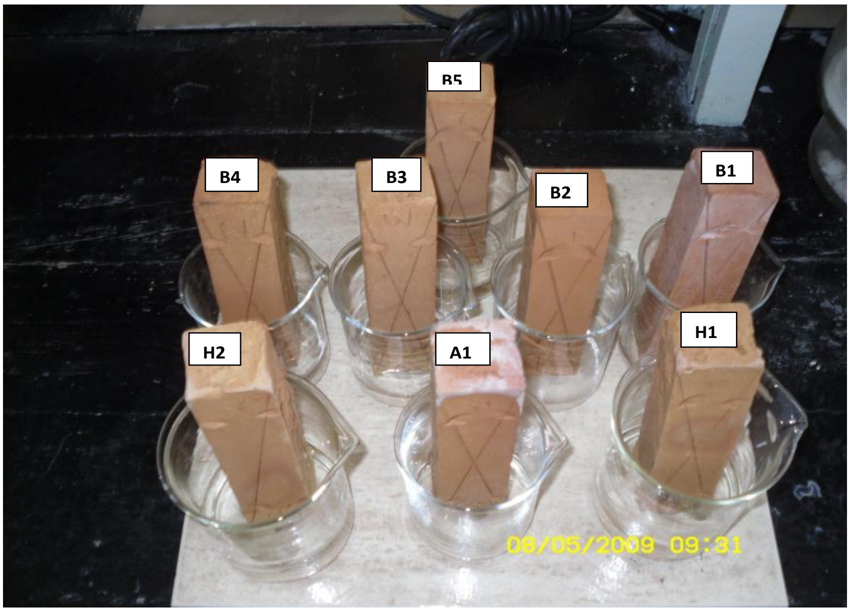

Figure 6. View of some of the prisms after the Efflorescence Qualitative test II

DISCUSSION AND CONCLUSIONS

The experimental results of three identification efflorescence tests are almost the same. The presence of barium sulphate precipitate in the aqueous extract of green pastes (Qualitative test I) shows that, the quantity of supplementary materials added ($BaCO_3$ or H_2O_2) is not sufficient to eliminate the efflorescence deposit, because in green pastes are yet sulphate ions.

The visually identification of efflorescence white powder in the fired prisms dipped in distilled water in 1/3 of their height for 48 hours (Qualitative test II), shows that there is the possibility of efflorescence occurrence in the ceramic products produced with the respective paste mix.

The high content of sulphate, sodium and potassium ions, as well as of the dry residue (which are accountable for efflorescence salts) in aqueous extract of fired pastes, shows that the quantity of supplementary materials added ($BaCO_3$ or H_2O_2) is not sufficient to eliminate all efflorescence deposit.

The results of the tests showed that, the addition of $BaCO_3$ above the stechiometric quantity minimizes the efflorescence deposit occurrence (Paste mixes B_4 and B_5).

The addition of H_2O_2 solutions in concentrations of 1 and 3 % and in ratios H_2O_2 solution/forming water of 1:1 and 0.5:1.5, used in the study were not sufficient to achieve good results in efflorescence minimizing. For all paste mixes H, where H_2O_2 solutions are used as supplementary material, the presence of barium sulphate and the efflorescence deposit occurrence were visually identified at the quality tests. The content of soluble salts in aqueous extract of fired pastes was high, too.

From the experimental results, it seems that the mixing time of the peroxyde solutions with the clay prior the shaping of products, has not any notable influence in the content of water soluble salts of fired products.

Quality chemical analyses of efflorescence white powder show that it contains especially sodium and potassium ions and only traces of barium ions. This means that the efflorescence deposits in the ceramic products produced with the clay used in this study are caused by the water alkaline sulphates.

REFERENCES

[1] F. M.Miler, J. M Melander, Efflorescence – A synopsis of the literature, Portland Cement Association, USA, 2003, pp.1-24

[2] H. B Newman, The efflorescence report, TechBullet 15, USA, 2009, pp.1-4

[3] US Patent 6548438, Method for processing ceramic materials, 2003, pp.1-15

[4] R. L. Kozikowski, P. F Taylor, G. F Miller, Development of accelerated tests method for measuring and minimizing efflorescence potential, Portland Cement Association, USA, 2007, pp.1-54

[5] M. Merrigan, Efflorescence: Cause and control, The Masonry Society Journal, USA, January-June, 1986, pp.1-4