

Efflorescence in a Conventional Wood Drying Kiln – A Case Study

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ABSTRACT

In newly built conventional wood drying kilns white deposits often occur on concrete construction parts during the process. These deposits occasionally cause confusion with investors for the reason they do not know whether deposits originate from wood or concrete. In this paper, inorganic origin of such deposits in a specific wood drying kiln has been affirmed. And additionally, efflorescence is discussed.

Key words: Ca⁺⁺; Deposits; Efflorescence; Hydrothermal Wood Processing; Mg⁺⁺; Na₂EDTA; Phenols

1. INTRODUCTION

1.1. Wood drying

Green wood after tree felling contains free water, which is mostly present within the dead cell cavities in liquid and vapour form, and bound water, which is mostly located in the amorphous regions of wood lignocellulosic matrix. The free and bound water has to be removed from wood in order to enhance its properties, stability, biological resistance and to prepare the wood for conventional final processing. Water can be removed from the wood through the variety of industrial drying methods and procedures, wherein the conventional wood drying process is the most commonly used. Conventional wood drying comprises water removal from wood matrix through forced moist air circulation at a desired and controlled air temperature and relative humidity, within the drying kilns of different construction.



Figure 1. Conventional (aluminium/concrete) wood drying kiln interior (photo: Klarić)



Figure 2. Infrared image of conventional wood drying kiln exterior, showing condensate and heat flow (photo: Klarić)

Modern structures of conventional wood drying kilns mostly consist of reinforced concrete floor and parapet with superstructure of corrugated aluminium panels filled with insulated material such as water repellent mineral wool as a walls and ceiling (Figure 1). Construction of new conventional wood drying kilns is usually carried out in a way that the investor prepare a reinforced concrete base, while the kiln producer provides and assembles aluminium components and other necessary segments. However, in many cases the final outcome of drying kiln construction is not adequate (Figure 2), which results in incapability to properly conduct the drying procedure, and to achieve appropriate dry wood quality, thus inevitably leads to higher production costs and to dissatisfied investor (Chrisholm and Adams, 2000).

1.2. Efflorescence

Efflorescence in chemistry is spontaneous loss of water by a hydrated salt, which occurs when the aqueous vapour pressure of the hydrate is greater than the partial pressure of the water vapour in the air, while their surface assume a powdery appearance (Encyclopaedia Britannica, 2015). In construction industry, efflorescence is a white (different colours are possible, depending on the type of salts) powdery or chunky deposits or stains of water-soluble salts left on the surface of masonry as the water evaporates, and usually appears shortly after the completion of construction (Merrigan, 2000). In generally, efflorescence is primarily aesthetic problem particularly where the decorative properties are very important, while it is not normally deleterious to long term concrete durability (Bensted, 2000; Dow and Glasser, 2003). In order to efflorescence appear, several conditions must be met (Merrigan, 2000):

- Water-soluble salts presence in any of the concrete component,
- Sufficient moisture presence in the structure to render the salts into a soluble solution,
- Presence of a path for the soluble salts to migrate through to the surface where the moisture can evaporate, thus depositing the salts which then crystallize and cause efflorescence.

In the conventional wood drying kilns, the main goal is to evaporate water from the wood without drying defects as quickly as possible, thereby microclimate conditions within kiln are always such that the circulating heated air is not fully saturated, having ability to absorb water evaporating from the wood surface. This means that in addition to the water evaporation from wood, the water will also evaporate from the concrete floor, as well. During the evaporation of water from concrete surface, physical migration of soluble salts and precipitation in the form of mostly white powdery or chunky mineral deposits occur, which is efflorescence respectively.

1.3. Problematics

In a wood processing company in the Republic of Croatia new conventional wood drying kiln was built. Investor built reinforced concrete floor and parapet in advance according to technical specification of kiln manufacturer, before kiln assembly. After first procedure of wood drying white chunky deposits appeared on floor inside of a kiln and on the outside of the parapet (*Figure 3*). The first question that has come up in wood processing company was: What happened, and are those deposits originate from the wood or from the concrete?



Figure 3. Efflorescence; on wood drying kiln floor (left and middle), on the outside of reinforced concrete parapet (right) (photo: Pervan)

Immediately after on-site inspection it was clear that the deposits does not originate from the wood but from the concrete. Regardless of the stated conclusion, on investor request, the efflorescence samples were taken from the kiln and were subjected to the laboratory analysis. The primary objectives of this research investigation were (1) to exclude organic origin, and (2) to confirm inorganic origin of white deposits within wood drying kiln, respectively. The simpler analytical methods were used in order to fulfil the set objectives, through a microscopic examination; Mg^{++} and Ca^{++} presence, and phenolics absence determination.

2. MATERIAL AND METHODS

2.1. Chemicals

For the analysis, chemicals were used without additional purification (*Table 1*). Deionised water (dH₂O) was prepared in a TKA/Thermo Scientific MicroMed Pure Water System (Type II according to ASTM D1193–06).

Table 1. Chemicals used in the research

Chemical	Producer / Country	CAS
Ammonia 25 %	Gram-Mol / Croatia	1336-21-6
EDTA disodium salt dihydrate	Kemika / Croatia	6381-92-6
Folin & Ciocalteu's phenol reagent 2M	Sigma-Aldrich / Germany	-
Gallic acid monohydrate, extra pure	Scharlau / Spain	5995-86-8
Kompleksin [®]	Kemika / Croatia	-
Murexide	Kemika / Croatia	3051-09-0
Sodium carbonate anhydrous <i>p.a.</i>	Lachner / Czech Republic	497-19-8
Sodium hydroxide <i>p.a.</i>	Lachner / Czech Republic	1310-73-2

2.2. Material

Samples of white deposits were obtained from newly build industrial scale conventional wood drying kiln concrete floor. Larger chunks of white deposits with yellowish surface, without any additional modification were sampled for the microscopic examination. For chemical analysis, sampled chunks of white yellowish deposits were milled and homogenized in an IKA A10 analytical mill in four milling passes per 30 seconds with 1 minute pause between each pass. Milled and homogenized sample was stored in glass jar till further analysis.

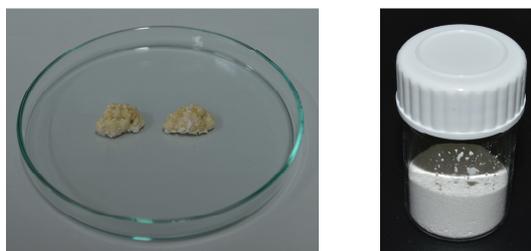


Figure 4. Deposit sample before milling (left), and after milling (right) (photo: Klarić)

2.3. Methods

2.3.1. Microscopy

Firstly, collected sample was analysed under the research light microscope (Axio Zoom V16, Zeiss), equipped with colour camera (AxioCam ICc 5). Images acquisition and evaluation were done with AxioVision SE64 (Rel. 4.9.1.) software. The analysis was conducted in order to examine sample surface structural characteristics.



Figure 5. Axio Zoom V16, Zeiss. LDG laboratory (photo: Klarić)

2.3.2. Determination of Mg^{++} and Ca^{++} ions in sample by EDTA titrimetric method

Since the great analytical precision for this research was not required, simpler EDTA complexometric titration of earth alkali ions (Mg^{++} & Ca^{++} exclusively) was applied. During sample stock solution preparation, 250 mg of milled and homogenized sample was dissolved in 500 mL of prepared dH_2O . During the dissolution of the sample in the dH_2O , solution within volumetric flask was subjected for 3 minutes in an ultrasonic bath (ELMA S15H) at room temperature, in order to achieve the complete dissolution. Ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) aqueous solution ($c = 0.05 \text{ mol}\cdot\text{L}^{-1}$) was prepared and stored in the glass bottle equipped with automatic burette (per Pellet, 25/0.05 ml, with Schellbach stripe). Sodium hydroxide 8 % (w/v) aqueous solution ($c = 2 \text{ mol}\cdot\text{L}^{-1}$) was additionally prepared. To determine sample stock solution Mg^{++} & Ca^{++} content, 50 ml of sample stock solution with addition of one kompleksin[®] pill and 2 mL of 25 % ammonia was immediately titrated in the Erlenmeyer flask with prepared EDTA solution (in quadruplicates). To determine sample stock solution Ca^{++} content, 50 ml of sample stock solution with addition of 2 ml of 8 % (w/v) NaOH (aq) and 0.2 g of murexide was immediately titrated in the Erlenmeyer flask with prepared EDTA solution (in quadruplicates). Both titration procedures were conducted on a magnetic stirrer (IKA RH BASIC 2), with the rotation in the same direction (mot 2), applying $6 \times 35 \text{ mm}$ PTFE coated magnet. Concentration of Ca^{++} was calculated by the equation (1). Molar concentration of Mg^{++} was obtained by subtracting Mg^{++} & Ca^{++} molar concentration with Ca^{++} molar concentration and calculated according to the equation (2).

$$Ca^{++} = \frac{\gamma_{(Ca^{++})} \cdot V_{ss}}{m_s} = \frac{\left(\frac{c_1 \cdot V_3}{V_0} \cdot M(Ca^{++})\right) \cdot V_{ss}}{m_s} [mg \cdot g^{-1}] \quad (1)$$

$$Mg^{++} = \frac{\gamma_{(Mg^{++})} \cdot V_{ss}}{m_s} = \frac{\left(\frac{c_1 \cdot V_3}{V_0} \cdot M(Mg^{++})\right) \cdot V_{ss}}{m_s} [mg \cdot g^{-1}] \quad (2)$$

$\gamma_{(x)}$ – mass concentration [$mg\cdot L^{-1}$]; V_{ss} – sample stock solution volume [L]; m_s – mass of the sample dissolved [g]; c_1 – the concentration of the EDTA solution [$mmol\cdot L^{-1}$]; V_0 – the volume of the test portion [mL]; V_3 – the volume of the EDTA used in the titration [mL]; $M(X)$ – molar mass.

2.3.3. Estimation of total soluble phenols (TSPs)

Total soluble phenols content was determined spectrophotometrically by Folin-Ciocalteu's method (Singleton and Rossi 1965; Scalbert *et al.* 1989) with some minor modifications. Three aqueous sample stock solutions with different concentrations were prepared (250, 500, and 1000 $mg\cdot L^{-1}$), and in each solution TSPs were determined in triplicates. Folin-Ciocalteu's phenol reagent aqueous solution (ten times folded), and sodium carbonate aqueous solution (75 $g\cdot L^{-1}$) were prepared. In 0.5 ml of aqueous sample stock solution 2.5 mL of prepared Folin-Ciocalteu's phenol solution was added and after 90 seconds 2.0 mL of prepared sodium carbonate solution was added. The mixture was then vigorously shaken for 5 seconds on vortex shaker (1000 min^{-1}). Incubation was conducted for two hours at room temperature. Calibration curve was obtained by dilutions of gallic acid aqueous stock solution (100 $mg\cdot L^{-1}$) at eight levels (0.0; 0.5; 1.0; 2.0; 4.0; 8.0; 16.0; 32.0 $mg\cdot L^{-1}$). The absorbance was measured versus a zero-absorbance reagent blank at 765 nm wavelength on Shimadzu UVmini 1240 single bean UV-Vis spectrophotometer. Concentration of TSPs was calculated according to equation (3). TSPs are expressed as gallic acid equivalents in milligrams of TSPs per gram of the sample.

$$TSPs = \frac{\gamma_{(TSPs)} \cdot V_{ss}}{m_s} = \frac{(ABS-b)}{m} \cdot V_{ss} [mg \cdot g^{-1}] \quad (3)$$

$\gamma_{(x)}$ – mass concentration [$mg\cdot L^{-1}$]; V_{ss} – sample stock solution volume [L]; m_s – mass of the sample dissolved [g]; ABS – absorbance [1]; b – y-intercept of linear equation; m – slope of linear equation

3. RESULTS AND DISCUSSION

Microscopic analysis has revealed the presence of crystalline formations on the surface of the studied sample. These findings are in accordance with initial expectations. Examples of obtained microscopic images at different magnifications are shown on *Figure 6*. Additionally should be mentioned that all efflorescence samples had hard solid structure.

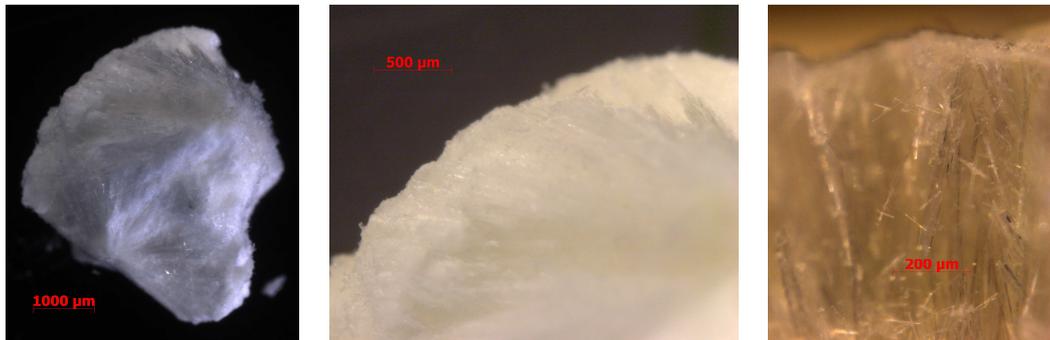


Figure 6. Efflorescence sample, magnification 12.5x (left), 32x (middle), 80x (right) (photo: Klarić & Španić)

By conducted complexometric titration with EDTA the presence of Ca^{++} and Mg^{++} ions has been confirmed. There was much higher concentration of Ca^{++} than Mg^{++} in the sample as can be seen in *Table 2*. As regards the elementary composition, wood is mostly composed of carbon, oxygen and hydrogen, while content of inorganic elements such as Na, K, Ca, Mg, Si is represented whit significantly less than 1 % (Ressel, 2007). According to the aforementioned, it is unlikely that amounts of Ca^{++} (~21 %) and Mg^{++} (~1.5 %) ions as obtained from the sample are leached from the wood.

Table 2. Amounts of the investigated cations in the sample

Cations	Number of measurements	Mean \pm SD	95 Confidence interval	Minimum	Maximum
Ca^{++}	4	209.42 ± 2.00	206.229 - 212.607	208.42	212.42
Mg^{++}	4	14.58 ± 0.00	14.583 - 14.583	14.58	14.58

As for calcium, Kresse (1987) reports that formed free soluble calcium hydroxide migrate to the concrete surface (only if the capillaries are fully filled with water) and reacts with carbon dioxide from the air which form water-insoluble calcium carbonate (*Figure 7*).

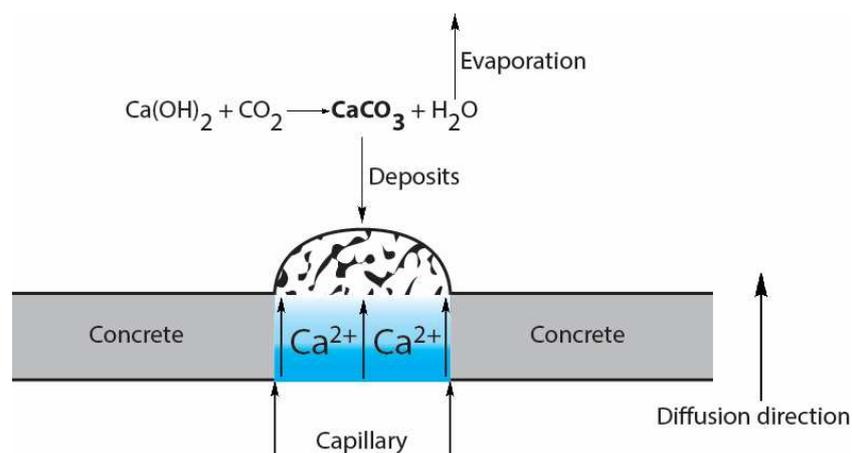


Figure 7. Schematic diagram of deposits formation on concrete surface (simplified according to Kresse, 1987)

By conducted UV-Vis spectrophotometric analysis it was determined that there is no soluble phenols (TSPs) present in the sample (*Table 3*). It can be observed (*Table 3*) that the concentrations of TSPs in milligrams per litre, and in milligrams per gram of a sample have negative numeric values. Stated arises due to the calculation method, via gallic acid calibration curve (*Figure 8*). Anyhow, as can be seen, values of obtained absorbances are zero. As well, it should be noted that applied spectrometric method was not optimized for this kind of a sample, and no prior study in relation to the type of sample has been conducted in this research. This is important to note because, the assay measures all compounds readily oxidizable under the reaction conditions and its very inclusiveness allows certain substances to also react that are either not phenols or seldom thought of as phenols (*e.g.* proteins) (Singelton *et al.*, 1999). For instance, inorganic ions Fe^{+2} , Mn^{+2} , I^- , S^{-2} , SO_3^{-2} show reactivity towards Folin-Ciocalteu reagent and thus can cause interference (Box, 1983; Everette *et al.*, 2010). Newer the less, assay results show that the investigated sample in our research did not contain such an interfering substances. Anyhow, the interference from inorganic and non-phenolic organic compounds are possible, in an inhibitory, additive or enhancing manner (Box, 1983; Dai and Mumper, 2010; Everette *et al.*, 2010). Therefore, in some cases it is possible that the sample could contain interfering substances which might even give false positive or somewhat lower result. As concerns phenols, they are most abundant wood metabolites, hence, that the investigated sample originates from the wood, it would contain at least some of the phenols.

Table 3. Total soluble phenols in the sample

Sample stock solution (aq) concentration [mg·L ⁻¹]	Number of measurements	Abs-765	Concentration	
		[1]	[mg·L ⁻¹]	[mg·g ⁻¹]
250	3	0.000 ± 0.000*	-0.16 ± 0.00*	-0.64 ± 0.00*
500	3	0.000 ± 0.001*	-0.13 ± 0.05*	-0.27 ± 0.09*
1000	3	0.001 ± 0.001*	-0.08 ± 0.08*	-0.08 ± 0.08*

*Mean ± SD

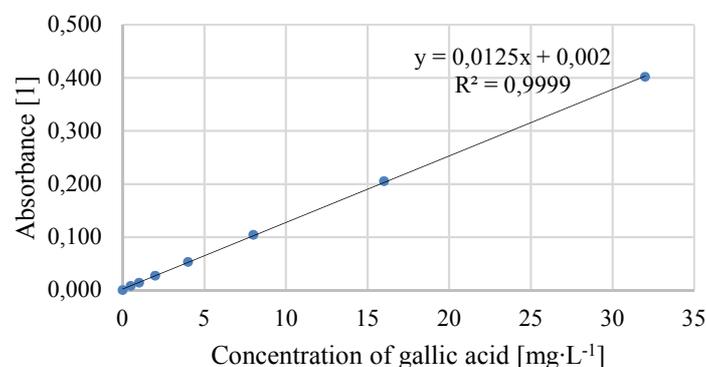


Figure 8. Obtained standard curve of gallic acid

Chemical composition of efflorescence deposits differ from case to case, and detailed chemical analysis of each efflorescence case should be conducted to determine its exact composition. In this research the intention was not to determine complete chemical composition of the sample, but to exclude biological origin of the sample through confirmation of some inorganic ions presence in higher amounts, than that would be expected wood to contain.

In generally efflorescence appears in a form of fine powdery deposits of water-soluble salts on masonry. But in conventional wood drying kilns, except in the form of fine powder (*Figure 9_{left}*, and *Figure 9_{middle}*), it can appear in a form of bigger chunks (*Figure 3*), because the evaporation of water is much greater, and the concrete is often rewetted (humidification, condensation, *etc.*) during wood drying process. Sometimes, during the process, while floor is wet efflorescence appears in a form of slimy and gooey mash (*Figure 9_{right}*).



Figure 9. Powdery deposits (left, middle); slimy and goeey mash (right) (photo: Pervan)

Efflorescence is considered to be only aesthetic problem in commonly masonry, however in wood drying kilns it could cause somewhat larger problems. When water-soluble salts are leached out, concrete becomes porous to some extent which enables additional moisture to enter and then concrete becomes susceptible to further degradation. Additionally, within the kiln, due to the drying of wood, different kinds of natural volatile compounds are emitted from the wood into the surrounding air, which are contained in water vapour and condensate as well (Pervan *et al.*, 2008). So this, mostly acidic moisture additionally damages concrete when it penetrates into the newly formed pores. In winter times, moisture contained in concrete pores is susceptible to freezing, and thus concrete micro cracks can occur. Such a surface weakened concrete floor is furthermore being damaged due to forklift movement and timber manipulation. Efflorescence appearance, however, cannot be 100 % prevented, but certainly can be minimized (Merrigan, 2000). During construction, sources of water-soluble salts should be minimized if possible. Water soluble salts can be present in any of the concrete components, such as cement, sand, water, or the soli under the kiln can be contaminated, and additionally water-soluble salts can be present in water which passes through concrete (if watertight insulation is not adequate). Regarding the water as a source of water-soluble salts, content of dissolved solids in the natural waters varies from place to place, as can be seen in *Table 4* for Croatia (mainly coastal belt).

Table 4. Parameters of water in some locations in the Republic of Croatia (Dadić, 2001)

Location	Electrolytic conductivity	Total dissolved solids	Salinity	Sum of earth alkali ions
	$\mu\text{S}\cdot\text{cm}^{-1}$	$\text{mg}\cdot\text{L}^{-1}$	1	$\text{mg}_{\text{CaCO}_3}\cdot\text{L}^{-1}$
Zagreb (Sesvete)	818	408	0.2	410
Slavonski brod	812	462	0.1	375
Mljet (Slatina – Kozarica)	5410	>2000	3.2	876
Vir (Lozice)	3160	1898	2	1296
Silba (Parenica)	12450	>2000	8.1	2004

To minimize efflorescence, additional care should be given during the construction of conventional wood drying kiln. Sand from a reliable source or washed sand should be used, and water with low content of solids and ions should be used, without exaggeration in free water content. Additionally, voids in mortar should be reduced to reduce capillary flow, by means of mechanical vibration. Most important, the transport of water through the structure towards the exposed surfaces should be hindered, whether by increasing the hydrophobicity with waterproofing admixtures and/or by lowering the permeability (Bensted, 2000). Concrete surface protective coatings are good solution, but which should be applied with regard to the conditions in which the structure is located, and according to strict manufacturer's instructions. Concrete structures within wood drying kilns are exposed to a broad range of chemical and physical reactions, as well as to different environments and influences. For instance, alternating wet and dry conditions, alternating hot and cold conditions, chemically aggressive environment, mechanical wear, exposure to freezing. All aforementioned influences should be taken into account when the wood drying kiln is being constructed.

4. CONCLUSIONS

1. In this particular case study, it has been determined that white deposits on a concrete structure of a wood drying kiln does not originate from wood, but it is inorganic origin. This inorganic matter is mineral deposits incurred from mineral migration to the concrete surface and loss of water. It is efflorescence.
2. Wood drying kiln concrete structures are exposed to different environments and influences, like alternating wet and dry, and/or hot and cold conditions, chemically aggressive environment, mechanical wear, exposure to freezing; therefore special care should be dedicated during the kiln construction.
3. Efflorescence in wood drying kiln is not just aesthetic problem, but it is a sign of badly and sloppily planned, supervised and executed construction work, accompanied by a long-term consequences on the compactness of the concrete structures.
4. The usage of concrete waterproofing admixtures and surface protective coatings is recommended to extend lifespan of the concrete floor.
5. Bad planning and small savings during drying kiln construction subsequently often cause difficulties in business like: dried wood defects, major repair expenses, employee stress, high energy consumption, *etc.*

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