

THE EFFECT OF PEAT COMPONENT CONTENT ON THE PROPERTIES OF FINAL PRODUCT IN ROOF TILE PRODUCTION

JONJAUA RANOGAJEC, RADMILA MARINKOVIĆ-NEDUČIN, RAJKO TOMANOVIĆ,
BRANISLAV ŽIVANOVIĆ*, SVETLANA RADOSAVLJEVIĆ**

Faculty of Technology, University of Novi Sad

**Institute for Testing of Materials, Beograd*

***Institute of Chemistry, University of Novi Sad*

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Prevention of scaling of roof tiles in the course of their service under diverse and changing atmospheric conditions is directly associated with control of the composition and characteristics of the raw material mixture. Since the scaling phenomenon is caused by the formation of an undesirable crystalline phase, the nature and dynamics of its development was studied in relation with the characteristics of a defined raw material mixture. Formation of the β -CaSO₄ · 0.5 H₂O crystalline phase was confirmed by comparative investigation of real systems, i.e. industrial samples exposed to definite atmospheric conditions, and model systems in laboratory tests. Interaction of the peat and carbonate components with montmorillonite clay in the closed system is considered to be the possible cause of the phenomenon observed.

Key words: roof tiles, open pores, acid rain, calcium sulphate modifications.

INTRODUCTION

The corrosion of roof tile caused by atmospheric effects is directly related to mineralogical composition of the starting raw material and parameters of the technological process [1, 2]. The scaling phenomenon results from degradation of the initial texture in the course of roof tile service [3, 4]. Efforts aimed at prevention of this negative phenomenon should be based on optimizing the raw material composition and preparation, together with ensuring the correct firing schedule for the respective well-defined mixture.

EXPERIMENTAL

Subject

The microstructural and textural properties of roof tiles were investigated in comparison with the tiles after one year of atmospheric exposure. Segments from different areas of each roof tile were analyzed, taking into account possible effects of internal stresses due to the tile forming process.

The layer model systems were prepared by pressing ($p = 1.5198$ MPa) a certain number of specimens of various compositions and firing them at 900 °C for 2 hours.

The model system was made from components present in the real raw material mixture, i.e. peat, calcium carbonate and montmorillonite clay.

Methods

- Scanning Electron Microscopy — SEM (Jeol ISM-35)
- Differential Scanning Calorimetry — DSC (Du Pont 1090)
- Mercury Porosimetry (Carlo Erba, type 1500), (max. pressure 151.98 MPa, $\Theta = 141.3^\circ$, $\gamma_{Hg} = 480 \times 10^{-3} \text{ N/m}$)

RESULTS AND DISCUSSION

The investigation of the microstructure of roof tile segments (Fig. 1) after exposure, with pronounced scaling, revealed the presence of flower-shaped crystals (Fig. 2), in the immediate proximity of open pores of critical size, as well as at the points of intimate contact between peat (Pt), carbonate (C) and montmorillonite particles (M), (Fig. 3). The phases were qualitatively determined by comparative SEM investigations of the pure components and the model system.

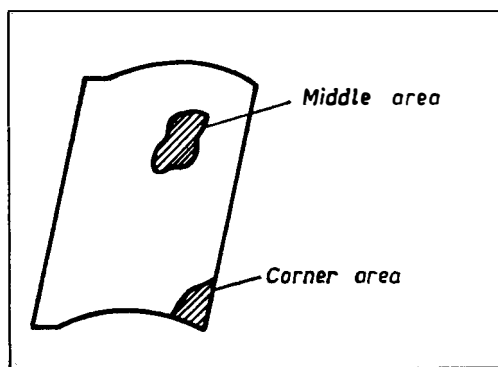


Fig. 1. Schematic diagram of roof tile with pronounced scaling areas (corner and center).

Comparison of the texture of tile segments exhibiting pronounced scaling with those having regular characteristics after exposure (intact specimens taken for analysis) showed a difference in pore size distribution (Fig. 4). A relatively high content of the critical pore size with respect to water condensation (radius range $0.12\text{--}0.25 \mu\text{m}$ [4, 5]) was found in the scaled sample (Fig. 2 and 4a); the pores are responsible for condensation of acidic rain with consecutive development of critical crystals during roof tile service. The phenomenon occurs particularly in segments with higher internal tension (corner and curved segments), (Fig. 1).

The investigation of fresh tiles showed them to contain the same type of crystalline phase even before exposure (Fig. 5). According to the conclusions drawn, nuclei of the critical phase are already present in the fresh tile structure and are subject to rapid growth by further reactions taking place under the conditions of atmospheric exposure.

The presence of calcium sulphate modifications was considered on the basis of the raw material characteristics and previous microstructural investigations.

Nuclei in the sulphate phase can be formed at the points of contact between the peat and carbonate components in the closed system with montmorillonite clay. The presence of the components was confirmed by detailed analyses of the raw material in its various layers of deposition.

This assumption was confirmed by model system investigations. In the preparation of model systems, the components present in real raw material were used, i.e. peat, calcium carbonate and montmorillonite clay. The following characteristic model systems were studied:

The model systems were exposed to acidic (SO_3 and SO_2) atmosphere for 45 days.

Microstructural investigation of samples of the carbonate layer (Fig. 6) showed the same critical acicular crystals (Fig. 7) to be present.

Besides the critical crystals mentioned, formation of another Ca-sulphate phase of lamellar type, surrounded by CaO phase, was observed (Fig. 8a). Comparative investigation (Fig. 8b) indicated the crystals to be $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.

The formation of the two types of Ca-sulphate crystals has been explained in the following way:

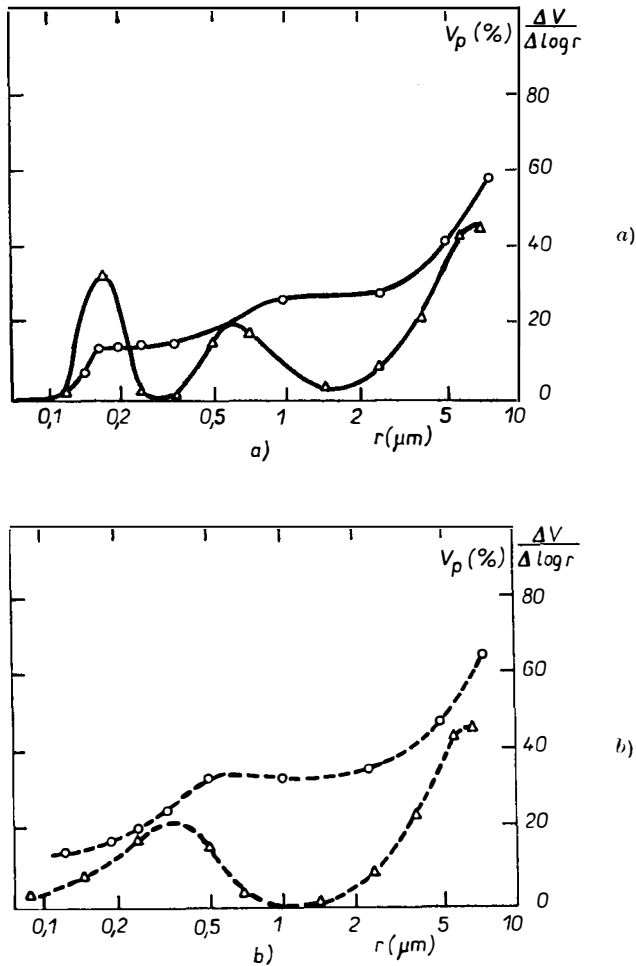


Fig. 4. Pore size distribution in a curved segment; a sample with pronounced scaling ($m = 0.754 \text{ g}$), b sample free of scaling ($m = 0.752 \text{ g}$).

The nuclei of the acicular Ca-sulphate phase are formed by the reaction of CaCO_3 and CaO with the high-sulphur gaseous phase originating from the peat component in the course of firing. In the enclosed system with montmorillonite clay, the presence of water enables formation of the hydrated Ca-sulphate form instead of the anhydrous one. The presence of nuclei is responsible for further rapid growth of the critical crystals in the acidic atmosphere.

The nature and extent of formation of the critical acicular crystals was studied by DSC analysis.

The DSC curves showed a pronounced exothermal effect in the temperature region of 300–320 °C (Fig. 9a), The effect is ascribed to transformation of $\beta\text{-CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$ to the α -form [5], the β -modification being present in the

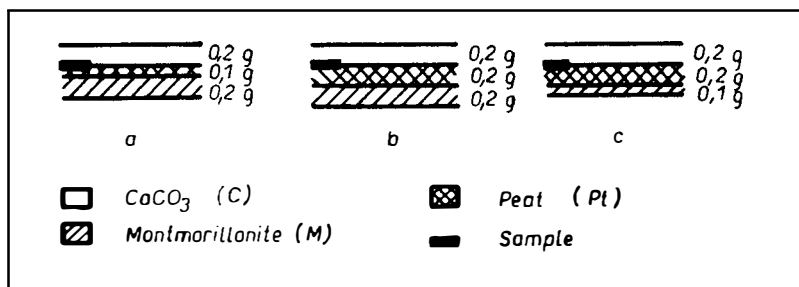


Fig. 6. The model systems a, b and c.

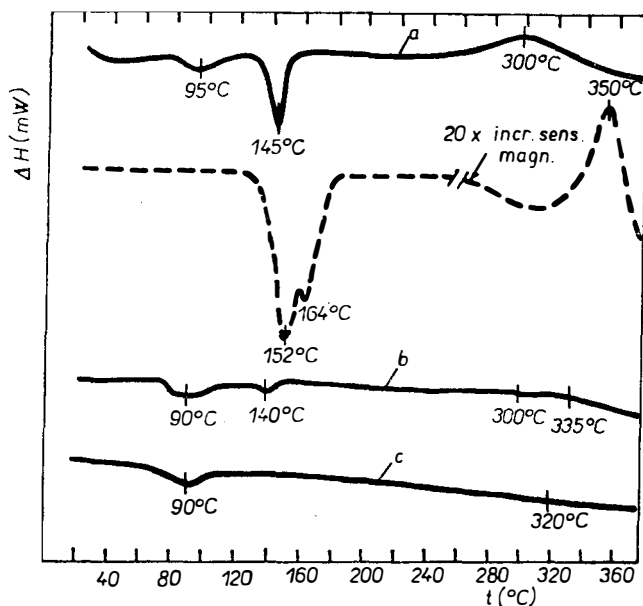


Fig. 9. DSC curves of the model systems (—) and $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ (-----).

original sample apart from small amounts of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. The conclusion was drawn on the basis of a different course of $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ transformation (Fig. 9b) with small quantities of $\beta\text{-CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ as one of the possible phases being formed.

CONCLUSIONS

The raw material characteristics, given by the content of peat, CaCO_3 and clay of the montmorillonite type allow nuclei of $\beta\text{-CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ acicular crystals to form in the course of tile firing. The presence of the nuclei is the main reason of extensive growth of this phase during exposure of the tile to acidic rain. The presence of critical-size pores responsible for capillary condensation contributes to the deterioration process called tile scaling in the course of long-term atmospheric exposure.

References

- [1] Hintz M.: *Ziegelindustrie International* 12, 649 (1983).
- [2] Eklinč A.: *Ziegelindustrie International* 12, 650 (1983).
- [3] Vasić R.: *Proceed. Yugoslav Meeting on Corr. and Degrad. of Building Materials*, Sput.
- [4] Budnikov P., Hewitonov F.: *Ceramic Materials for Corrosive Environments* (in Russian), Strojizdat, Moscow 1952.
- [5] Belyankin S., Ivanov V., Lapin V.: *The Petrography of Technical Stones* (in Russian), Izdat. Akad. Nauk USSR, Moscow 1952.

VLIV OBSAHU RAŠELINOVÉ SLOŽKY NA VLASTNOSTI PÁLENÉ STŘEŠNÍ KRYTINY

Jonjuana Ranogajec, Radmila Marinković-Nedučin, Rajko Tomanović, *Branislav Živanović,
**Svetlana Radosavljević

Technologická fakulta, Univerzita v Novém Sadu

**Ústav pro zkoušení materiálu, Bělehrad*

***Katedra chemie, Univerzita v Novém Sadu*

K zabránění odprýskávání pálené střešní krytiny v průběhu jejího použití v širokém spektru atmosférických podmínek je nutno zaměřit se na řízení složení a vlastností surovinové směsi. Jelikož odprýskávání je působeno tvorbou nežádoucí krystalické fáze, studovalo se její složení a dynamika jejího vzniku ve spojitosti s vlastnostmi dané surovinové směsí. Srovnávacím měřením reálných systémů, tj. průmyslových vzorků aplikovaných v definovaných atmosférických podmínkách a modelových systémů v laboratorních podmínkách byla jako hlavní příčina odprýskávání zjištěna tvorba krystalových zárodků nové krystalické fáze. Kontakt rašeliny, CaCO_3 a CaO nebo rašeliny a CaO s montmorillonitickým jílem, přispívající ke vzniku uzavřeného systému, umožňuje tvorbu krystalových zárodků $\beta\text{-CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ jehlicovitého habitu v průběhu výpalu. Přítomnost nukleje je základní příčinou pokračujícího růstu této fáze v průběhu vystavení pálené krytiny kyselým deštěm. Přítomnost pórů s kritickým průměrem, umožňujících kapilární kondenzaci, přispívá k pozorovanému jevu, jenž se projevuje odprýskáváním při použití krytiny.

- Obr. 1. Schéma střešní krytiny s oblasti výrazného odprýskávání (roh a střed).
Obr. 2. SEM rohové oblasti střešní krytiny, p — otevřený pór.
Obr. 3. SEM rohové oblasti střešní krytiny, C — CaCO_3 , Pt — rašelina, M — montmorillonitický jíl.
Obr. 4. Rozdělení velikosti pórů v zakřivené oblasti; a) vzorek s výrazným odprýskáváním ($m = 0,754 \text{ g}$), b) vzorek bez odprýskávání ($m = 0,752 \text{ g}$).
Obr. 5. SEM nepálené krytiny v rohové oblasti, CS — siran vápenatý, C — CaCO_3 .
Obr. 6. Modelové systémy: a, b, c.
Obr. 7. SEM vzorků s vrstvou uhlíkatanu vápenatého, modely a, b, c.
Obr. 8a. SEM tabulkovitých krystalů v modelových systémech.
Obr. 8b. SEM krystalů $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ (čistá fáze).
Obr. 9. Křivky DSC modelových systémů (.....) a $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ (.....).

ВЛИЯНИЕ СОДЕРЖАНИЯ ТОРФЯНОГО КОМПОНЕНТА НА СВОЙСТВА ЖЖЕНОЙ КРОВЛИ

Полюана Раногаяц, Радомила Маринкович-Недучин,
Райко Томанович*, Светлана Радосавлевич**

технологический факультет Университета, Нови Сад

*Научно-исследовательский институт испытания материала, Београд

**кафедра химии Университета, Нови Сад

Для предотвращения отслаивания жженой кровли во время ее использования в широком спектре атмосферных условий приходится уделять внимание управлению состава и свойств сырьевой смеси. Отслаивание вызывается образованием нежелательной кристаллической фазы и поэтому исследовали ее состав и динамику ее образования в зависимости от свойств данной сырьевой смеси. С помощью сопоставительных измерений реальных систем, т. е. промышленных образцов, применяемых в установленных атмосферических условиях и модельных систем в лабораторных условиях было установлено в качестве основных причин отслаивания образование кристаллических зародышей новой кристаллической фазы. Контакт торфа, CaCO_3 и CaO или торфа и CaO с монтмориллонитическим илом, поддерживающий образование закрытой системы, предоставляет возможность образования кристаллических зародышей $\beta\text{-CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$ игольчатого габита во время обжига. Присутствие зародышей является основной причиной продолжающегося роста данной фазы в жженой кровли, подвергаемой при использовании кислым дождем. Присутствие пор с критическим диаметром дает возможность капиллярной конденсации и таким образом вызывает наблюдаемое явление, проявляющееся в отслаивании используемой кровли.

- Рис. 1. Схема кровли с областью резкого отслаивания (угол и середина).
Рис. 2. SEM угловой области кровли, p — открытая пора.
Рис. 3. SEM угловой области кровли, C — CaCO_3 , Pt — торф, M — монтмориллонитический ил.
Рис. 4. Распределение размера пор в искривленной области:
a образец с резким отслаиванием ($m = 0,754 \text{ g}$),
b образец без отслаивания ($m = 0,752 \text{ g}$).
Рис. 5. SEM нежженой кровли в угловой области, CS — сульфат кальция, C — CaCO_3 .
Рис. 6. Модельные системы: a, b, c.
Рис. 7. SEM образцов со слоем углекислого кальция, модели a, b, c.
Рис. 8a. SEM листовых кристаллов в модельных системах.
Рис. 8b. SEM кристаллов $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ (чистая фаза).
Рис. 9. Кривые DSC модельных систем (.....) и $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ (.....).

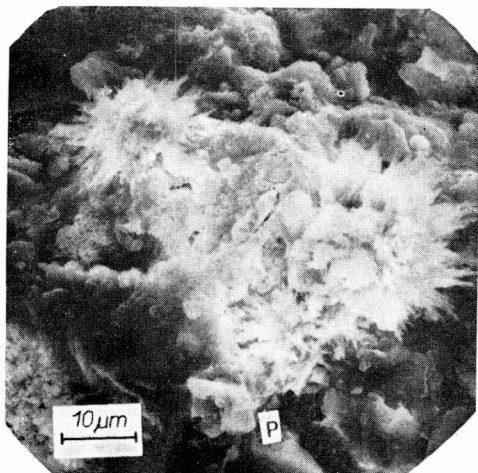


Fig. 2. SEM micrograph of roof tile corner segment, p — open pore.

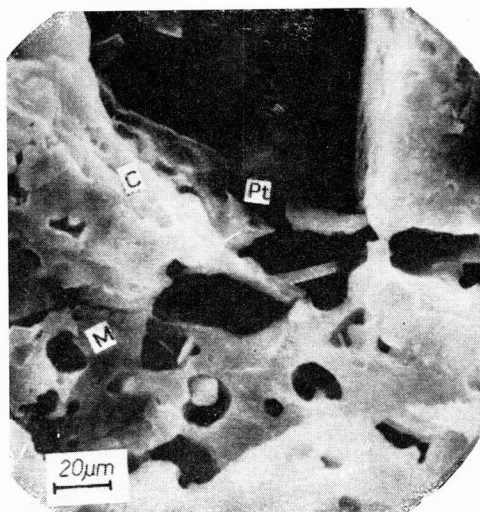


Fig. 3. SEM micrograph of roof tile corner segment, C—CaCO₃, Pt — peat, M — montmorillonite clay.

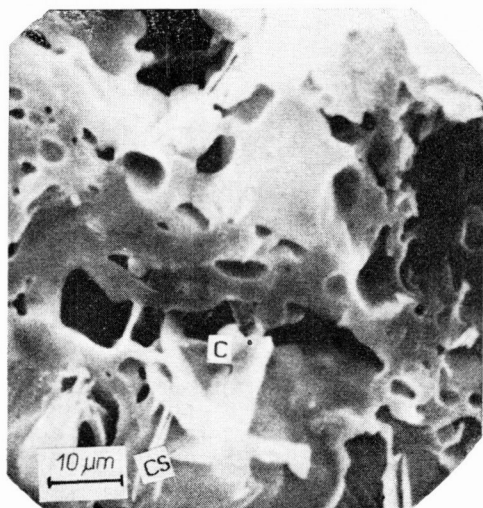


Fig. 5. SEM micrograph of a fresh roof tile corner segment; CS — calcium sulphate, C—CaCO₃.

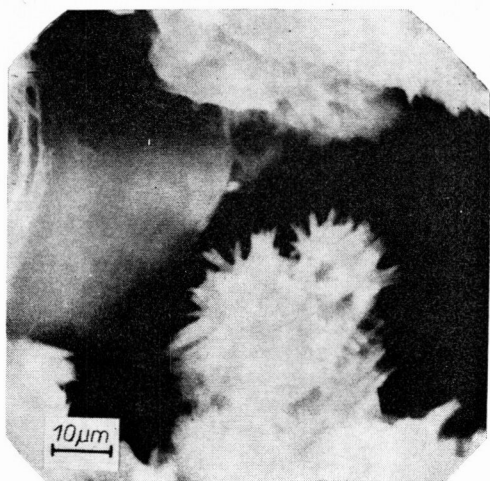
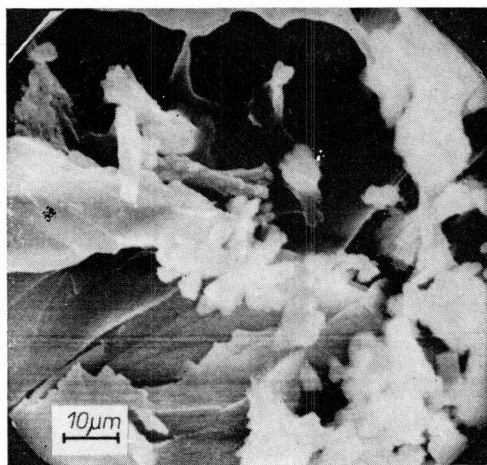
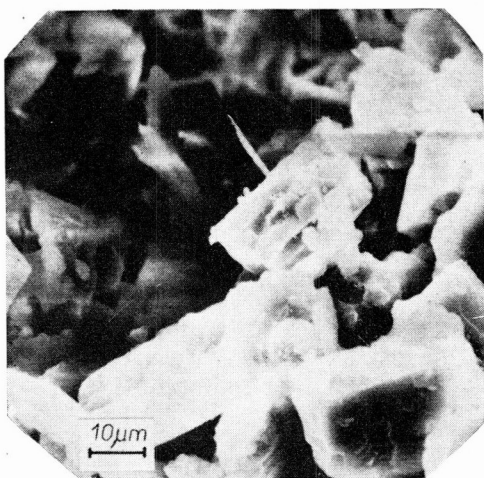


Fig. 7a.



b)



c)

Fig. 7. SEM micrograph of carbonate layer samples, models a, b and c.

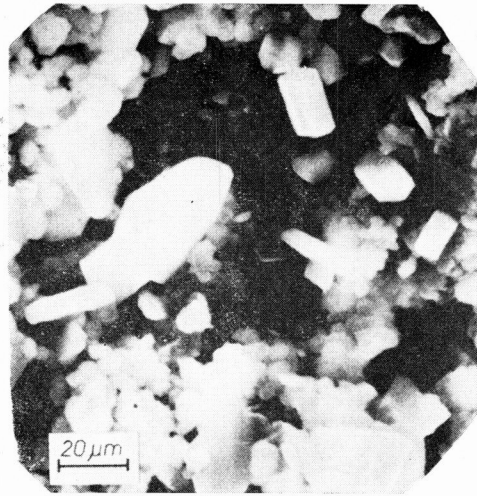


Fig. 8a. SEM micrographs of lamellar-type crystals in the model system.

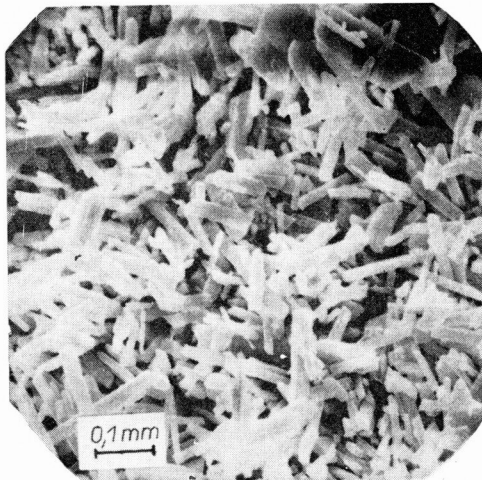


Fig. 8b. SEM micrographs of the CaSO₄ · 2 H₂O crystalline phase (pure phase).