The 55th International October Conference on Mining and Metallurgy
15 - 17 October 2024, Kladovo, Serbia
https://ioc.irmbor.co.rs

DOI: 10.5937/IOC24047R Original Scientific Paper-Mineral Proccesing

STRUCTURAL STABILITY OF CALCITE MINERAL AFTER SURFACE MODIFICATION

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Abstract

Calcite was modified with stearic acid in the "wet" and "dry" process. The results showed that the total hydrophobicity is achieved at a concentration of stearic acid 1.5% in the "wet" process, and 3% for "dry". Microscopic analysis is in accordance with the degree of coating obtained. On the basis of the infrared spectra, it was concluded that there was no change in the position and intensity of most strip of modified calcite relative to the starting sample. The X-ray diffraction analysis showed that the calcite after modifying stearic acid retains its basic structure.

Keywords: *limestone, calcite, X-ray, IR, microscopic analysis*

1. INTRODUCTION

The limiting factor in the application of limestone as a filler in the polymer industry is its hydrophilic surface, as such incompatible with the hydrophobic polymer surface. Recent development trends polymer industry are aimed at increasing the limestone which is the most abundant mineral calcite surface-modified procedures. The surface modification of calcite as the main mineral in limestone, organic modifier types of surfactants, can significantly improve the quality of limestone as a filler for use in the polymer industry [1-5].

2. EXPERIMENTAL

Material: The experimental studies, presented in this paper, have used a sample of limestone deposits "Venčac"-Arandjelovac (Serbia).

Test methods: Stearic acid is used for calcite modification of limestone as the main minerals.

The process of "wet" (S) and "dry" (D) modification of calcite (C), and the method of determining the degree of coverage were described by the authors in previously published work [6, 7, 8].

X-ray diffraction analysis: Samples were recorded on a diffractometer brand "Philips", model PW-1710, with a curved graphite monochromator and scintillation counter. The intensities of diffracted X-ray radiation Cu (λ=1.54178 Å) were measured at room temperature at intervals of 0.02° 2θ (diffraction angle θ), for 2.5 s, and the range of 2θ from 4° to 65°. The X-ray tube is loaded with a voltage of 40 kV and current of 30 mA, slotted for routing the primary and diffracted beam of about 1 and 0.1 mm.

Infrared spectroscopy: Subsamples were recorded in 4000-250 cm^{-1} on a device "Perkin Elmer 983 G" and prepared in the form of KBr pill by mixing 1% of sample with 99% KBr.

Mineralogical analysis: The polarization was performed under a microscope for transmitted light rebound made by the "Jenapol-in" company of Carl Zeiss Jena, immersion method, to identify the present minerals. The immersion liquid is xylene for the initial sample of limestone and samples modified the stearic acid water. Zoom lens is 3,2 to 20X.

3. RESULTS AND DISCUSSION

Chemical composition: The chemical composition of the starting sample is shown in Table 1. Based on CaO, obtained by the chemical analysis (54.77%), and assuming that all the MgO (0.79%) associated with dolomite, was obtained by calculation that sample is 95.84% $CaCO_3$.

Table 1. *Chemical composition of limestone "Venčac" Aranđelovac*

Component	**CaO**	**Fe_2O_3**	**Al_2O_3**	**MgO**	**SiO_2**	**Na_2O**	**K_2O**	**LoI***
Content, %	54.77	0.084	0.035	0.79	0.24	0.027	0.0036	44.05

*****loss on ignition (LoI)

Coating degree: By determining a degree of coverage as a measure of hydrophobicity achieved samples, it was found that the impregnation of 99.9% for the "wet" modification process gets stearic acid at concentration of 1.5% (sample CS-1.5), and "dry" procedure in stearic acid concentration of 3% (sample CD-3). Comparative diagrams are shown in Table 2.

Table 2. *Coating degree modification of calcite samples*

Stearic acid, %	**0.5**		**1**		**1.5**		**2**		**3**		**4**	
Process	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**
Coating degree,%	65.5	55.5	93	90	**99.9**	96.5	99.9	98	99.9	**99.9**	99.9	99.9

X-ray analysis: At the beginning, the X-ray analysis was carried out with the calcite samples of modified samples in which there was full hydrophobicity of both procedures CS-1.5 and CD-3, Figure 1.

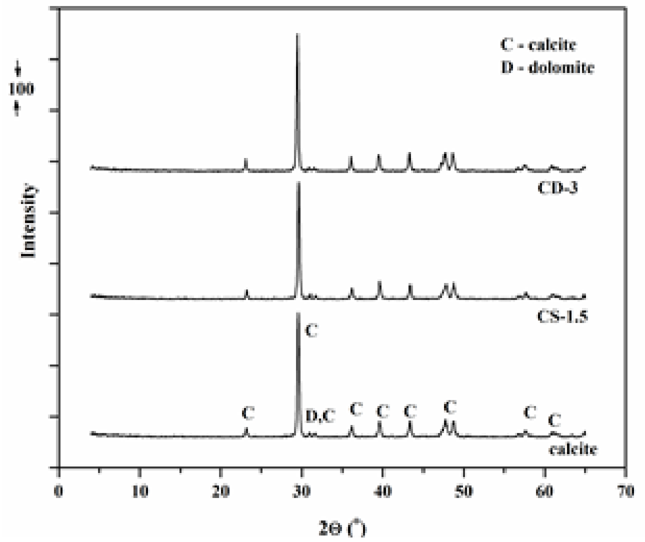
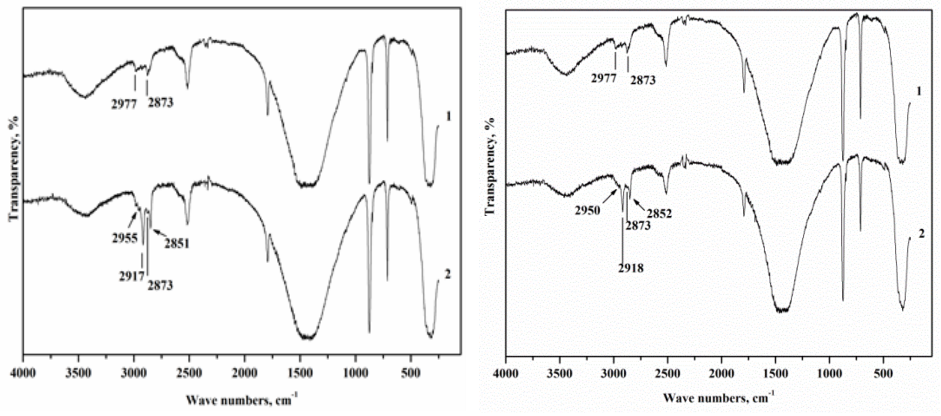


Figure 1. *Comparative X-ray diffraction patterns of sample flow and calcite samples, modified CS-1.5 and CD-3*

The XRD analysis showed that there was no violation of the crystal structure of calcite in the "wet" and "dry" process of modification, which is expected to be given by the adsorption process with its place at the phase boundary.

Infrared spectroscopy: The infrared spectroscopy and infrared spectra, shown in Figure 2, were carried out at the beginning with the calcite samples of modified samples CS-.5 and CD-3.



a) b)

Figure 2. *a) Comparative infrared spectra of: 1) initial sample of calcite, 2) sample CS-3; b) Comparative infrared spectra of: 1) initial sample of calcite, 2) sample CD-3*

The Infrared spectroscopic analysis (Figure 2a) showed that the "wet" calcite modification of stearic acid at concentration of 3% (sample CS-3) do not change the positions and intensities of the fundamental bands, characteristic for the mineral calcite. In the area of 3000 cm $^{-1}$ to 2800 cm $^{-1}$, there are more bands and more tape on the neg of initial sample, due to the symmetric and asymmetric valence vibration of CH bond of the hydrocarbon chain of the adsorbed organic compounds. In doing so, calcite treated with stearic acid (CS-3), the bands shifted to slightly higher wave numbers compared to the bands of crystalline stearic acid, indicating a greater presence of vertical orientation (trans conformation of the hydrocarbon chain) and denser, "packing" of hydrocarbon chains on the surface of minerals.

Compared to the typical flow of starting calcite (spectrum 1) notes that there has been no change in the position and intensity of most strip of modified calcite CD-3 (spectrum 2), Fig 2b. Considering the modified sample CD-3 (spectrum 2), as well as sample CS-3 (Fig. 2a, spectrum 2), in the 3000 to 2800 cm^{-1} bands are observed at 2950, 2918, 2873 and 2852 cm^{-1}, originating from the valence vibration of CH bond in -CH_3 and-CH_2 - groups of hydrocarbon chains of the adsorbed organic compounds [3, 5]. However, it can be seen that the bands of valence vibrations of CH-CH_3 group less pronounced than in the sample CS-3, obtained by the "wet" modification. When the wave number IR CH vibration band in the spectrum of 2, compared to the lanes that Osman and Suter [5] observed in the spectrum of crystalline stearic acid (2954, 2916, 2872 and 2849 cm^{-1}), it can be seen that the bands in calcite, treated with stearic acid in the "dry" process, (CD-3), slightly shifted towards higher values, except for the bands corresponding to the asymmetric CH vibration of -CH_3 group (2950 cm^{-1}). This shift to the lower wave numbers and valence bands are small, CH vibration-CH_3 group, indicating better representation of hair (Gauch) conformation and orientation of the hydrocarbon chain of hair on the calcite surface, and less dense "packing" of hydrocarbon chains the adsorbed layer of CD-3.

Microscopic analysis: The microscopic analysis was carried out with samples of calcite and calcite coated completely, received the "wet" process (CS-1.5) and "dry" process (CD-3), Figure 3. On micro flow pattern of calcite (Fig. 4a). It becomes apparent on a micro flow pattern of calcite (Figure 3a) that the free calcite grains have the characteristic interference colours of a high order, characteristic for the fair-faced mineral calcite.

On micro sample CS-1.5 (Figure 3b) and CD-3 (Figure 3c), the of water is observed as a means of immersion, aggregates coated with the hydrophobic particles of calcite.

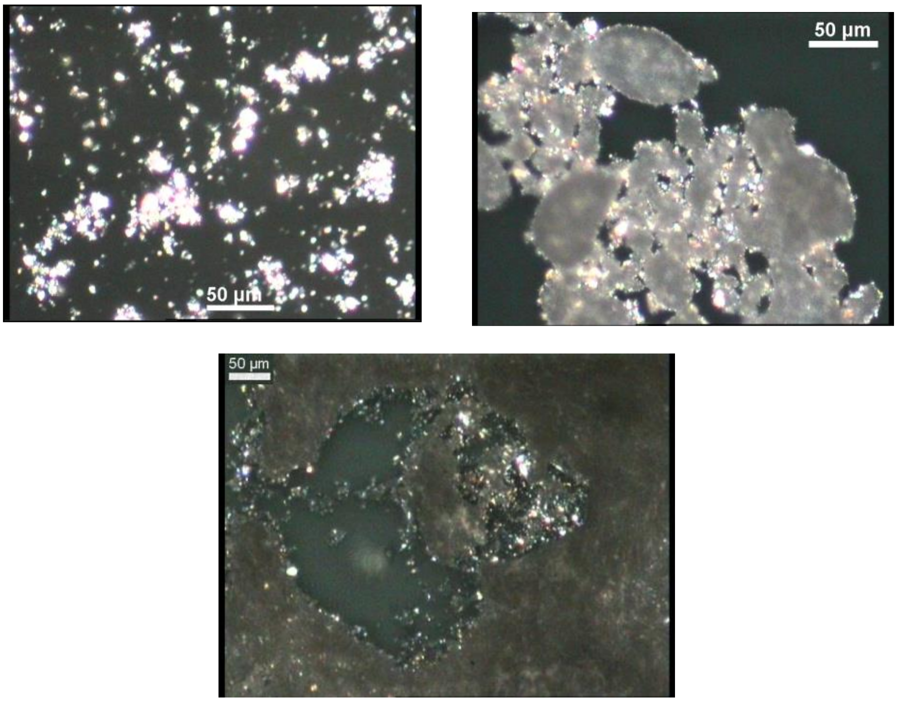


Figure 3. *Micrographs: a) initial calcite, b) CS-1.5 (magnification 20X), c) CD-3 (magnification 10X)*

4. CONCLUSION

The results presented in this paper showed the following: Full calcite coating with the "wet" modification process was obtained at concentration of stearic acid 1.5% (sample CS-1.5), and in the "dry" process of stearic acid at concentration of 3% (sample CD-3). The X-ray diffraction analysis showed that the modification does not violate the crystal structure of minerals. The infrared spectroscopic analysis and "wet" and "dry" modified calcite showed that the modification does not change the positions and intensities of the fundamental infrared band characteristic for calcite. The presence of stearic acid-modified of calcite was confirmed by the microscopic analysis, since they occur very strong form aggregates.

ACKNOWLEDGMENT

The authors would like to thank the Ministry of Science, Technological Development and Innovation of the Republic of Serbia for supporting the research (Grant No: 451-03-66/2024-03/200023).

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