

TRANSFORMATION OF VATERITE INTO CALCITE IN THE ABSENCE AND THE PRESENCE OF COPPER(II) SPECIES

Thermal analysis, IR and EPR study

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(Received December 30, 2002; in revised form May 08, 2003)

Abstract

The transformation of vaterite into calcite may be performed by heating in the presence and the absence of oxygen. Vaterite remains thermally stable until a calcination temperature of 450°C. It transforms progressively to calcite up to 500°C giving two exothermic peaks: 1) at 481°C due to the transformation of vaterite surface which is in contact with a small amount of calcite phase already formed with the time on the solid surface from the humidity atmosphere; 2) at 491°C due to the transformation of pure vaterite bulk. The calcite phase remains stable until 700°C. Above this temperature the formation of CaO is observed.

Keywords: calcite, copper, IR and EPR, thermal analysis, vaterite

Introduction

Vaterite and calcite are two different forms of calcium carbonate (CaCO_3). The first possesses a rhombohedral structure whereas the second is an orthorhombic structure. It is well-known that vaterite transforms into calcite either by simple contact with water at room temperature [1–7] or by heating under air [8–10]. The introduction in the vaterite metal ions can stabilize or delay its transformation into calcite. This phenomenon was obtained when vaterite was doped by Cu^{2+} ions [11–14]. In fact, by a simple washing of vaterite with water, it transforms rapidly into calcite. When this washing is done with Cu^{2+} solutions, the transformation depends on the Cu^{2+} concentrations. For a low copper concentration (10^{-4} M L^{-1}) a certain delay in the transformation process is observed whereas, for 10^{-4} M L^{-1} of Cu^{2+} ions, the vaterite remains stable with time. For a 10^{-2} M L^{-1} solution, a mixture of vaterite, aragonite cubic calcite and malachite is obtained after the transformation process.

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The purpose of this work is to study the transformation of vaterite into calcite in function of calcination temperature. This study was performed in the absence and the presence of Cu^{2+} in vaterite.

Experimental

Cu^{2+} /vaterite samples with different copper(II) concentrations were prepared by adding 10^{-2} M L^{-1} of $\text{Cu}(\text{NO}_3)_2$ solutions to a known amount of vaterite (2 g per 0.5 dm^3). These latter solutions were shaken to obtain homogeneous carbonate phases at 293 K. The samples were filtered and dried at room temperature.

Thermal analysis measurements were performed using a Netzsch STA 409 equipped with a microbalance, differential scanning calorimetry (DSC) and a gas flow system. Vaterite was treated under a flow of dry air (75 mL^{-1}). Temperature was raised at a rate of 5°C min^{-1} from room temperature to desired temperatures.

The specific areas of solids are determined by the BET method using a Quantasorb Junior apparatus, and the gas adsorbed at -196°C is pure nitrogen.

Infrared (IR) spectra are scanned on a Perkin Elmer FTIR 1600 model spectrophotometer. The pressed samples are obtained using KBr disks, each one containing 1.5 mg sample and 120 mg KBr.

The electron paramagnetic resonance (EPR) measurements are performed at 77 and 293 K on a Varian E9 spectrometer. A cavity operating with a frequency of 9.3 GHz (X-band) is used. The magnetic field is modulated at 100 kHz. Precise g values are determined by comparison with a reference sample ($g=2.0028$).

Results and discussion

Thermal analysis study

Figure 1a illustrates the TG and DSC curves of the pure vaterite sample after heating the solid under a flow of dried air. The DSC curve reveals four exothermic peaks at 216, 381, 481 and 491°C and an endothermic peak at 785°C . The exothermic peaks were obtained without any mass loss. On the contrary, the endothermic peak was accompanied with a large mass loss (44%). This loss corresponds exactly to the decomposition of CaCO_3 solid into CaO and CO_2 .

When vaterite is impregnated by a copper(II) solution (10^{-2} M L^{-1}), only one DSC exothermic peak at 498°C was observed. Whereas, no modification was noticed for the endothermic peak at 785°C (Fig. 1b). In order to understand, on one side, the absence of two exothermic peaks at 216 and 381°C and on the other side, the replacement of the two exothermic peaks at 481 and 491°C by one at 498°C , pure vaterite has been heated under a nitrogen flow. As in the case of copper/vaterite, the first two exothermic peaks (216 and 381°C) were not observed. Whereas, the two other exothermic peaks (481 and 491°C) and the endothermic peak were obtained at the same temperatures applied under air (Fig. 1c). From these results, it is obvious to deduce that the two exothermic peaks obtained at 216 and 381°C under air are closely corre-

lated to the interaction between oxygen and the vaterite surface. Consequently, when vaterite is impregnated by a copper(II) solution, a Cu^{2+} ions layer is formed on the vaterite surface preventing the interaction between this latter phase and oxygen.

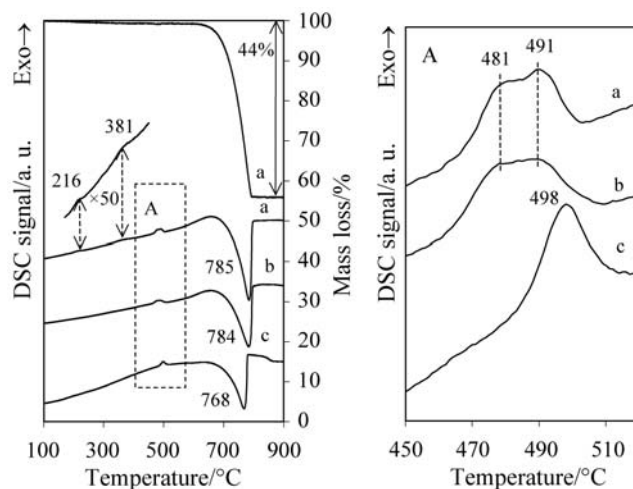


Fig. 1 TG and DSC curves of a – pure vaterite under air; b – pure vaterite under nitrogen and c – copper containing vaterite under air

The two exothermic peaks obtained at 481 and 491 °C can be unambiguously attributed to the transformation of vaterite into calcite. Indeed, in numerous studies [8–10], an exothermic peak has been obtained and not two as in our case in the same domain of temperatures when vaterite is calcined under a flow of air. This single peak has been attributed to the transformation of the calcium carbonate structure from the vaterite phase into the calcite phase. In addition, it has been demonstrated that the transition temperature is strongly dependent on the sample preparation and the heating rate. In order to explain the presence of two exothermic peaks, IR and EPR studies of the solid were performed on pure vaterite and copper/vaterite in terms of calcination temperature.

IR results

Figure 2 shows the IR spectra obtained after calcination vaterite at different temperatures under air.

The bands obtained for the untreated solid at 745, 876 and 1089 cm^{-1} are characteristics of pure vaterite [11–14]. A band at 712 cm^{-1} with a weak intensity was present. This band is due to the presence of small amounts of calcite. When the calcination temperature increased from room temperature up to 450 °C, the intensities of the above bands do not change. Whereas, the intensity of the bands attributed to vaterite decreased between 450 and 490 °C and disappeared above 490 °C (Fig. 3). In parallel, from a calcination temperature of 450 °C, the band intensity at 712 cm^{-1} characteristic

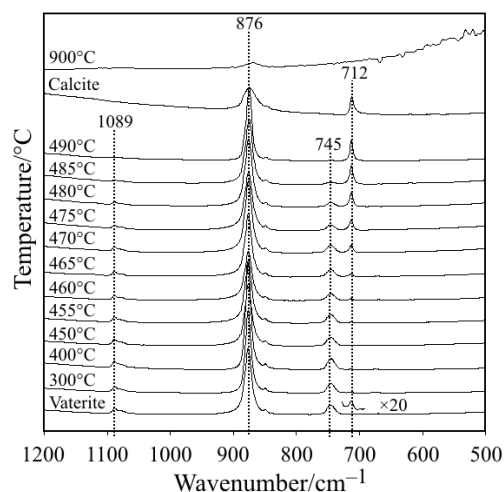


Fig. 2 IR spectra of vaterite calcined at different temperatures under air

of calcite, increased between 450 and 490°C to reach a plateau. The bands obtained on the new spectrum (712 and 876 cm^{-1}) are characteristics of pure calcite [11–14]. When vaterite is calcined at temperatures higher than 800°C, the IR spectrum obtained is characteristic of CaO phase. The formation of this phase is related to the decomposition of calcite at high temperatures. Similar IR spectra were obtained for copper/vaterite. No trace of bands corresponding to CuO phase was identified.

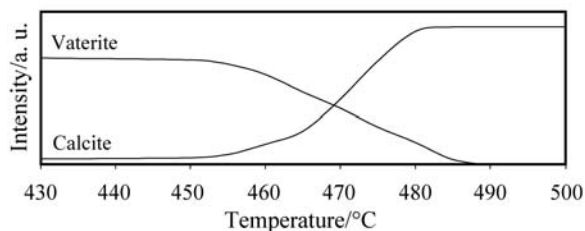


Fig. 3 Variation of the concentration of vaterite and calcite phases vs. the calcination temperature

In conclusion, the IR results have evidenced the presence in the untreated vaterite of a small amount of calcite. When vaterite is heated under air from room temperature to 490°C, only the calcite phase was obtained. The same phenomenon was obtained in the presence of copper.

EPR study

Figure 4 shows the EPR spectra obtained when copper/vaterite was calcined at different temperatures. For pure vaterite, no EPR signals were evidenced. All the signals

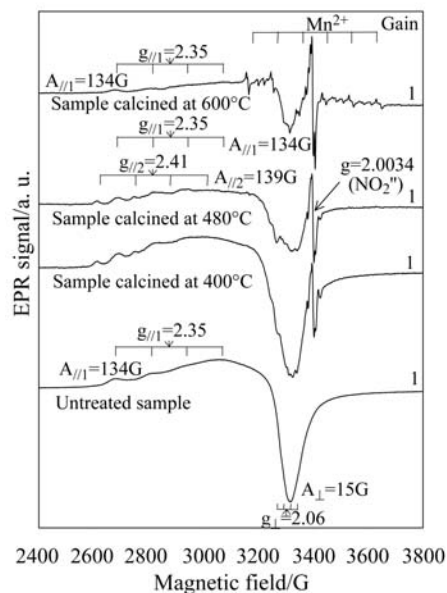


Fig. 4 EPR spectra of copper containing vaterite calcined at different temperatures

observed on copper/vaterite samples correspond, without ambiguity, to isolated and clusters of Cu^{2+} ions [15–18].

For the untreated sample, an EPR signal with the EPR parameter values $g_{\parallel 1}=2.35$, $g_{\perp 1}=2.06$, $g_{\text{iso}1}=2.16$, $A_{\parallel 1}=134$ G and $A_{\perp 1}=15$ G was obtained. This signal can be attributed to isolated Cu^{2+} ions located rather on the vaterite surface than in the bulk since the EPR parameter values indicate that the Cu^{2+} ion sites possess an octahedral symmetry surrounded by less than six ligands [19–21]. The number of ligands confirms that the Cu^{2+} ions are located on the vaterite surface.

When copper/vaterite is calcined under air up to 500°C , a new EPR signal appeared with the first one. This new signal characterized by $g_{\parallel 2}=2.41$, $g_{\perp 2}=2.06$, $g_{\text{iso}2}=2.18$, $A_{\parallel 2}=139$ G and $A_{\perp 2}=15$ G was also attributed to isolated Cu^{2+} ions located in sites slightly different from the first ones but with an octahedral symmetry surrounded by six ligands [19–21]. These sites seem to be located in the vaterite phase. Indeed, since the EPR signals obtained on the untreated vaterite and the calcite phases have the same EPR parameter values, this means that on the surface of the untreated vaterite the calcite phase already exists. This calcite phase has been formed with time by simple contact of the vaterite surface with the humidity of air [1–7]. The small amount of this phase was evidenced with IR results. When vaterite was calcined at 250°C , the Cu^{2+} ions of the surface diffuse in the bulk and are located effectively in vaterite sites which gave the new EPR signal. Indeed, the intensity of this signal remained stable up to 450°C while the vaterite structure is stable, then the intensity decreased during the transformation of vaterite into calcite and finally disappeared after

the total transformation ($>500^{\circ}\text{C}$). The disappearance of the new signal and the diminution in the intensity of the first one are probably due to the formation of CuO particles undetectable by EPR since they possess strong dipolar interactions [21]. The formation of CuO in calcite is favored because the specific area of this latter ($1\text{--}4\text{ m}^2\text{ g}^{-1}$) is lower than that of vaterite ($17\text{ m}^2\text{ g}^{-1}$).

In addition, a well-resolved signal centered at $g=2.0034$ is obtained with a hyperfine structure of three components. This latter signal was attributed to NO_2° radical [22, 23]. The origin of this radical is probably due to the decomposition of copper nitrate precursor of Cu^{2+} ions after calcination. The NO_2° signal remained stable at higher temperatures but a signal characteristic of Mn^{2+} ions [11–14], present in the solid, as impurities, appeared.

From the above results, it is now possible to give an interpretation for the presence of both exothermic peaks at 481 and 491°C instead of one during the transformation of vaterite into calcite. Indeed, Peric *et al.* [8] have demonstrated that the presence of calcite in vaterite favors the phase transformation towards low temperatures. Consequently, in our untreated vaterite, calcite was present on the surface in small amounts creating two types of vaterite: the first one, vaterite which is directly in contact with the calcite phase and the other one can be considered as pure because it is far from the calcite phase. The presence of these two types can lead to the appearance of the two exothermic peaks at 481 and 491°C . The first peak corresponds to the transformation of vaterite situated nearby the calcite whereas, the second one corresponds to the transformation of the pure vaterite.

Conclusions

Vaterite used in this work was not pure but doped with a small amount of calcite. This latter phase seems formed with the time from the humidity atmosphere. Therefore, it is present rather on the surface than in the bulk. The presence of calcite in a small amount creates two types of vaterite: the pure vaterite in the bulk and the vaterite/calcite on the surface. These two vaterite types are responsible of the two exothermic peaks obtained at 481 and 491°C during the transformation of vaterite into calcite by calcination. The presence of copper in vaterite does not delay the transformation like it was obtained when this solid is in contact with the pure water. This can be due to the presence of copper on the vaterite surface and not in the bulk.

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The authors would like to thank the 'Conseil Général du Nord', the 'Région Nord-Pas de Calais' and the European Community (European Regional Development Fund) for financial supports in the EPR and the thermal analysis apparatus purchase.

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