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REACTIONS OF CALCITE IN WATER IN THE PRESENCE OF STEARIC ACID[***]

Abstract

In the suspension of water and calcite, with pH 10.14, on the border of calcite / water was formed a double electric layer. Its structure, or hydrophilic properties of minerals, depended on the concentration of potential determination ions, Ca^{2+} i CO_3^{2-}, pH of the environment, and the adsorption of water molecules and ions (and molecules), formed in a suspension of calcite as a result of its solubility in alkaline media. The structure of such a way formed electrical double layer, influenced on interaction of minerals with stearic acid as a surface of active substance. In the presence of stearic acid, the pH value of slurry decreased to 8.72 due to the dissociation of stearic acid in alkaline medium and reaction of neutralization. As the result of dissociation, in the suspension, besides the un-dissociated acid molecules, there were also stearine ions $CH_3(CH_2)_{16}COO^-$, (St^-), which have reacted with the surface of minerals, transforming it from hydrophilic to hydrophobic.

Keywords: calcite, stearic acid, solubility, electric double leyer

INTRODUCTION

Name of pure calcite is derived from the Greek word cals, which means slaked lime. By chemical composition, it is $CaCO_3$, hardness per Moss-3 and very brittle. The density of the pure mineral is 2.72 kgm⁻³, and if it contains impurities, density varies from 2.7 kgm⁻³ to 2.85 kgm⁻³. Its brightness is glassy, and according to the fissile planes can be noticed the overflow of color. Calcite is transparent to milky. When it is clean and totally colorless, it is called the icelandic calcite. It is usually white, but can be colored differently: bluish, grayish yellow, greenish, reddish, etc. Calcite is relatively easily to soluble during the atmospheric precipitation and surface water when it can be converted to calcium bicarbonate $Ca(HCO_3)_2$, which is significantly more soluble than calcium carbonate [1]. Calcite has rhombohedral crystallisation. In the nature, a large number of crystal forms (300) exist. The crystals were generally prism or rhomboeder or skalenoeder shaped, which one are the most common. In some cases of calcite forming, the skeletal crystals arise. It occurs in the form of stalactites, then like coarse to fine grain and compact calcite [1].

EXPERIMENTAL PART

Material and methods

A sample of limestone is used in the experimental tests from THE deposit "Venčac" -AranDJelovac. The characterization of this sample showed that the dominant mineral is calcite (> 95%), so due to this, in the further discussion of results, instead the term calcite shall be used instead the term limestone. To obtain the acidic medium is used stearic acid, $CH_3(CH_2)_{16}COOH$, by technical grade, produced by the firm "Fluka" - Switzerland. For acid dissolving was used chloroform $CHCl_3$, p.a>99%, produced by „Centrohem" - Stara Pazova.

Process for preparing the suspension for testing. In 500 ml of distilled water heated to 50°C (temperature measured by thermometer), with vigorous stirring, 50 g of a limestone (calcite) sample was added which resulted obtaining 9.1% suspension. Weight of stearic acid in 6 samples, calculated on 100 g of calcite was: 0.5 g; 1 g; 1.5 g; 2 g; 3 g and 4 g. Apropos stearic acid was added into 100 g of calcite, its concentration is expressed in the phr units (phr- parts per hundred parts of resin). Mixing time of suspension was 15 minutes at a given rpm of mixer which is 1500 r/min.

Procedure of determination Ca^{2+} ions in the aqueous suspension of calcite. In 50 ml of water heated at 50°C, 5 g of calcite was added and mixed with stirring machine 1min, and then, the suspension was centrifuged. Ca^{2+} ions are determined in resulting filtrate.

For mixing the suspension was used a laboratory mixer model "RE 166", manufacturer "Janke & Kunkel" - Germany, which has a range from 50 to 6000 r/min. The chemical composition of limestone and content of Ca^{2+} ions in filtrate from suspension is determined on the atomic absorption spectrophotometer, type "Perkin Elmer 703 Analyst 300".

RESULTS AND DISCUSSION

Chemical composition of the starting sample of limestone

Based on the CaO content, obtained by chemical analysis of a limestone sample (54.77%), and assuming that all the present MgO (0.79%)is related to dolomite, it was found by computation that a sample has 95.84% $CaCO_3$. According to the division of limestones, the starting pattern belongs to a class of pure limestone, because it contains more than 95% $CaCO_3$, and less than 1.2% MgO, [2].

Reactions of the calcite in aqueous solutions

To define the composition of saturated aqueous solution of calcite, it is necessary to take into account three groups of equilibrium chemical reactions [3]. These reactions are:

1. Equilibrium chemical reactions of carbonate species in the suspension of calcite and water

$$(g) + \quad \rightleftarrows \qquad (1)$$
$$\rightleftarrows \quad + \qquad (2)$$
$$\rightleftarrows \quad + \qquad (3)$$
$$+ \qquad (4)$$

2. The balance of ion pairs

$$+ \quad \rightleftarrows \qquad (5)$$

$$\qquad (6)$$

$$\rightleftarrows \qquad (7)$$

3. The balance of solid-liquid

$$\qquad (8)$$

The composition of saturated solution of calcite can be opened or closed related to the atmosphere. In the open system, solution is balanced with partial pressure

of CO_2, $p(CO_2)$, equation 1, while in the closed system there is no exchange CO_2 with the atmosphere. The pH of solution can vary by addition the acids or bases as well as changing $p(CO_2)$.

Distribution of ions and molecules in the closed and open system calcite / water

Distribution of ions and molecules that occurs in indoor and outdoor system calcite/water and distribution the chemical species of saturated aqueous solution of calcite in equilibrium with the atmosphe-ric CO_2, $(p(CO_2) = 1.36 \times 10^{-4}$ bar) at 25°C are shown in Figures 1a, 1b and 1c [4]. It is observed that on distribution of chemical species it has a significant influence of pH and $p(CO_2)$ as well as the mutual reactions of chemical species. Dependence of share the chemical species of saturated aqueous solution of calcite from $p(CO_2)$ in the closed and open system according to the atmosphere is shown in Figures 1a and 1b. Figure 1c shows a diagram of chemical species of saturated aqueous composition of calcite for composition balanced with atmospheric $p(CO_2)$.
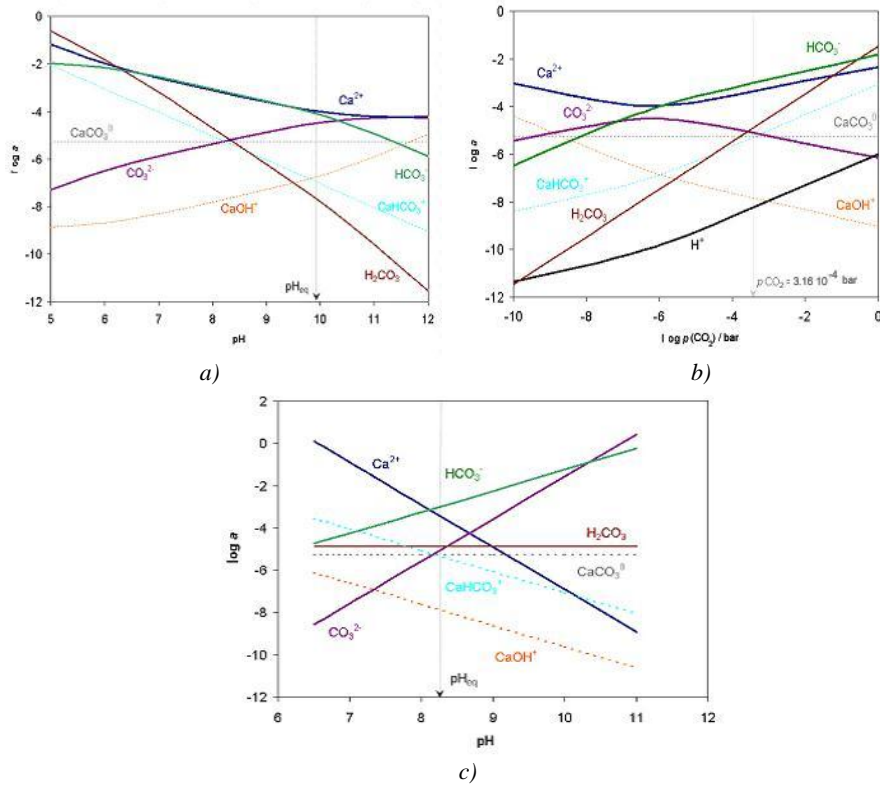

a)

b)

c)

Figure 1 *Distribution of ions and molecules in the closed (a); in open (b) system calcite/water and species distribution diagram for saturated calcite/water system in equilibrium with atmospheric CO_2 ($p(CO_2)=1,36 \cdot 10^{-4}$ bar), at 25°C (c)*

It can be seen on diagrams shown in Figure 1a that increasing pH of solution reduces the share of   and   ions, and increases the proportion of   ions.

During the equilibrium of pH (pH = 9.9), in the suspension dominate   and   ions while   are present to a lesser extent. It can be seen on diagrams shown in

Figure 1b that reducing $p(CO_2)$ increases the pH of solution as a result of reduction the concentration of carbonic acid. Decreasing p (CO_2) from 1.0 to 1.58x10^{-7} bar, the equilibrium pH increased from 6.0 to 11.3. At the pH <10.5, in solution are dominated and   ions, whereas   ion is presented in the lesser extent. When the pH increases from 6 to 10.5, the equilibrium concentration from   increases, and at the same time reduces the concentration   and   but they are still dominant in the suspension. At the pH> 10.5 starts dominance   ions with increasing ions in order to keep the charge balance. From diagrams shown in Figure 1c, it can be seen that the activity of   is not pH dependent and it is defined according to the reaction (1). In the open system during the constant pCO_2 $(p(CO_2)=1.36x10^{-4}$ bar) by addition of acid/base (HCl/NaOH), the pH of solution does not change. Adding the base takes to the higher concentration of negatively charged ions, mainly   i   , while adding the acid increases the concentration of positively charged ions, mainly   .

Interphase calcite-water

Many researchers dealt by the interphase calcite-water. So, Hansen and his associates [5] concluded that the presence of water on the calcite surface reaction takes place according to the following equation:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^-$$

(9)
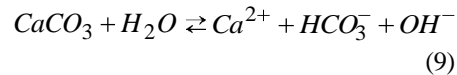
As a result of this process, the calcite suspension becomes alkaline. Using the results of Foxall and associates [6], these authors have pointed out that in calcite, ions that determine the electrokinetics properties are calcium ions and carbonate ions, rather than H$^+$ and OH$^-$ ions. These ions, apropos pH of the environment, only determine which chemical species dominates in solution: CO_3^{2-}, HCO_3^- or H_2CO_3. Determining the presence of Ca^{2+} ions in the aqueous suspension of calcite, which was used in the assays presented in this paper, 12 mg of Ca^{2+}/liter is obtained. According to some literature data about the contact calcite and water, a double electric layer is formed that is shown in Figure 2 [7].
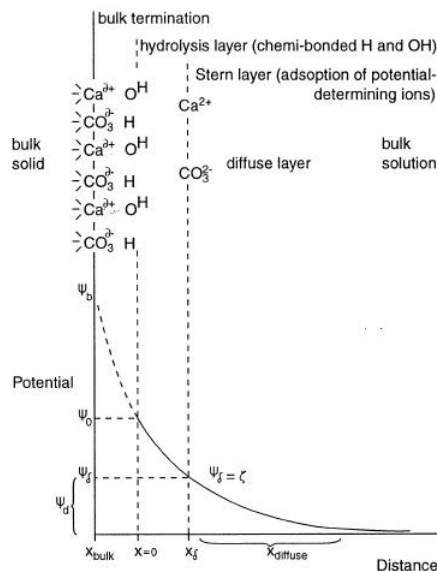

Figure 2 *Model of double electrical layer of calcite on the interface mineral/water [7]*

According to this model, where electrical double layer is in contact calcite with water, directly along the boundary surface of mineral, which consists of Ca^{2+} and CO_3^{2-} ions, there are located, due to the hydrolysis reaction, the chemisorbed H^+ and OH^- ions. These ions compensate the excess positive or negative charge on the surface of calcite. With formed chemisorbed layer, calcium ions and CO_3^{2-} ions are absorbed in the Stern layer. These ions are responsible for electrokinetics properties of calcite minerals. When the chemisorbed layer of H^+ and OH^- ions is removed then Ca^{2+} and CO_3^{2-} ions from the Stern layers again become an integral part of the three-dimensional crystal lattice of calcite. The tests presented in this paper showed that calcite is mineral which belongs to the type of salt and is water soluble. In the resulting aqueous suspension may take place and the specific reactions and form the different ions and molecules of carbonic acid, which the concentration depends on concentration of dissolved CO_2, and , also, pH of the solution (Figure 1a, 1b, 1c). From the results which are presented in this paper, 9.1% suspension of the starting calcite sample by specific surface area of 4.8 m^2/g had a pH of 10.14 (Figure 3). Based on values of the alkaline pH suspension, it was concluded that dominated are the reactions which leads to increasing the concentration of hydroxyl ions in solution, reaction 10:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^-$$
$$(10).$$
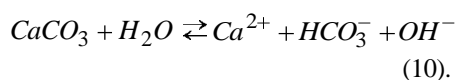
On the border of calcite/water is forming a double electric layer, whose struc

ture apropos hydrophilic properties of minerals, depends on concentration of potential determination of ions, Ca^{2+} and CO, dissolved CO_2 and pH of solution (concentration of H^+ and OH^- ions) and adsorption of formed ions (and molecules) in solution, that are towards the distribution diagram (Figures 1a, 1b, 1c) dominant in the alkaline medium. The structure of such a formed electrical double layer still affects the interaction of minerals with surfactant (stearate ions and molecules of stearic acid), which should lead to hydrophobization of mineral surfaces.

Reactions of calcite in the presence of stearic acid

According to the literature, adsorption of stearic acid on natural calcite usually takes place in a nonpolar solvent, because the calcite dissolves in water and pH of aqueous medium influence to its solubility, and also to the degree of dissociation of stearic acid. However, Hansen et al. showed that the treatment of calcite with water before addition stearic acid into the n-decane improves the adsorption of stearic acid on the calcite surface [5]. In order to monitor the behavior of calcite in the presence of stearic acid with different concentrations of stearic acid, the pH of each solution was measured after separation the solid phase. The results were compared with the pH value of 9.1% suspension of calcite, which amounts to 10.14. Curve of depending pH value of solution from the concentration of stearic acid is shown in Figure 3.
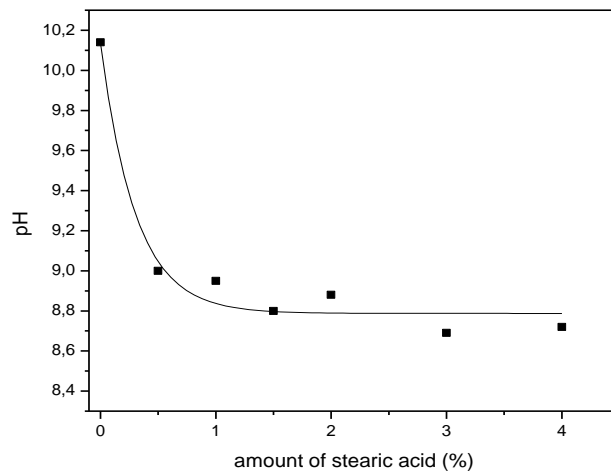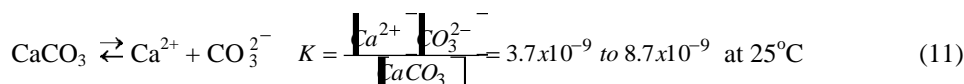
**Figure 3** *The pH value of the solution in function of concentration of stearic acid*

It can be seen that the pH 9.1% of aqueous suspension of calcite is 10.14 and in the presence of low concentration of stearic acid (0.5 phr ≈ 0.5%) leads to decrease the pH value of solution at pH = 9.00. With further increase of concentration of stearic acid, further weakly decrease of the pH value can be noticed (during the concentration of stea ric acid 1 phr, the pH is 8.95, and at concentration of 4 phr ≈ 3.9%, pH is 8.72). Characteristics of calcium carbonate in an aqueous solution have been studied by many researchers [8]. The dissociation constant of calcite at 25°C is in the order of 10^{-9} and it is separated according to the reaction 11.

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K = \frac{\left[Ca^{2+}\right]\left[CO_3^{2-}\right]}{\left[CaCO_3\right]} = 3.7x10^{-9} \; to \; 8.7x10^{-9} \; at \; 25^oC \quad (11)$$

A suspension of calcite/H$_2$O has, according to some published data the pH about 9 [9], depending on partial pressure of CO$_2$. In the aqueous suspension of calcite may occur according to the reactions 1-8 different ions and molecules of carbonic acid, whose concentration depends on the concentration of dissolved CO$_2$, and pH of solution. Based on the literature data, it can be assumed that even at the border calcite/water in 9.1% sus- pension, used in these studies, also forms an electric double layer, but in it dominate ions by distribution diagram at pH = 10.14 which are present in a given system. So, 9.1% suspension of calcite has pH = 10.14 (Figure 3), which is higher than pKa of stearic acid (pKa = 5.7), after addition into this suspension of stearic acid solution in non-polar solvent where its dissociation acts:

$$CH_3(CH_2)_{16}COOH \rightleftharpoons CH_3(CH_2)_{16}COO^- + H^+ \quad (12)$$
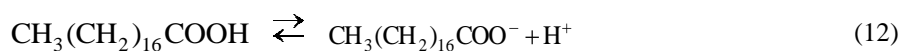
As a result of stearic acid dissociation, the concentration of H$^+$ ions grows, also the concentration of CH$_3$(CH$_2$)$_{16}$COO$^-$, stearate ion (St$^-$). The results in this paper fortified that, by the fact that there is decrease of the pH value of solution after addition, even low concentration of stearic acid from 0.5% (pH = 9.00), apropos until the neutralization reaction.

Isoelectric point (pH at which the zeta potential is 0) in some samples of calcite is pH = 11.4. Anionic surfactants (surface active agents) can be adsorbed from solution with lower pH values, however, in an acidic medium, CaCO$_3$ decompose with formation of CO$_2$, water, and Ca^{2+} ions. According to Martinez-Luevanos and coworkers [10], the reaction between protons and CaCO$_3$ occurs at pH 8.3, so at pH 8 is achieved the best balance between these two reactions. The results obtained in this study showed that in the presence of stearic acid, pH of the suspension decreases (Figure 3). At concentration of 0.5 phr $\approx$ 0.5% the pH value of the suspension was 9.00, whereas at concentration of 4 was 8.72 phr. Since the pKa of stearic acid (pKa = 5.7) is less than the pH of 9.1% suspension of calcite (pH = 10.14), the decrease in pH value can be explained, as already mentioned, by dissociation of stearic acid in an alkaline medium by reacting neutralization.

CONCLUSION

For observing the reactions of calcite in water, 9.1% suspension was used whose pH was 10.14. For testing the reaction in an acidic medium is used a precisely ordered mass of stearic acid, 0.5 g; 1 g; 1.5 g; 2 g; 3 g and 4 g of added per 100 g of the calcite. Solubility of calcite in water depends by dissolved CO$_2$ and pH of the environment. Suspension of calcite, used for the tests, had pH = 10.14. Based on the alkaline pH value of suspension, it can be concluded that in the suspension are dominated reactions which leads to increasing the concentration of hydroxyl ions, like the reaction, for example: $CaCO_3 + H_2O$ $\rightleftarrows Ca^{2+} + HCO_3^- + OH^-$. On the border of calcite/water, a double electric layer is formed. Its structure, apropos, hydrophilic properties, are dependent from the concentration of potential determination ions, Ca^{2+} and CO, pH value of the environment, and adsorption of molecules of water and ions (and molecules) formed in this suspension due to its solubility. The structure of such formed electrical double layer, further influenced on the minerals interaction with surface-active substance (a stearate ion and molecule of stearic acid). In the presence of stearic acid, the pH value of slurry decreased. At concentration of 0.5 phr, the pH value was 9.00 and at 4 phr it was 8.72. Bearing in the mind that the pKa of stearic acid (pKa = 5.7) is lower than pH of calcite suspension of calcite (pH = 10.14), the decrease of pH value can be explained by dissociation of stearic acid in an alkaline medium and neutralization reaction. As a result of this, dissociation of stearic acid occurs in alkaline environment, and neutralization reaction. Like consequence of stearic acid dissociation and neutralization reaction, in suspension, besides non dissolved molecules, ions of stearate CH$_3$(CH$_2$)$_{16}$COO$^-$, (St^-) were in certain concentration which reacted with the surface of minerals transformed it from hydrophilic to hydrophobic form.

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REAKCIJE KALCITA U VODI I U PRISUSTVU STEARINSKE KISELINE[***]

Izvod

U suspenziji kalcita i vode, čiji je pH 10,14, na granici kalcit/voda formirao se dvojni električni sloj. Njegova struktura, odnosno hidrofilne osobine minerala, su zavisile od koncentracije potencijal određujućih jona, Ca^{2+} i CO_3^{2-}, pH sredine i adsorpcije molekula vode i jona (i molekula) formiranih u suspenziji kalcita usled njegove rastvorljivosti u alkalnoj sredini. Struktura tako formiranog dvojnog električnog sloja je uticala na interakciju minerala sa stearinskom kiselinom kao površinski aktivnom materijom. U prisustvu stearinske kiseline pH vrednost suspenzije je opadala do 8,72 zbog disocijacije stearinske kiseline u alkalnoj sredini i reakcije neutralizacije. Kao posledica disocijacije u suspenziji su se pored nedisosovanih molekula kiseline nalazili u određenoj koncentraciji i stearatni joni $CH_3(CH_2)_{16}COO^-$, (St^-) koji su reagovali sa površinom minerala prevodeći je iz hidrofilne u hidrofobnu.

Ključne reči: *kalcit, stearinska kiselina, rastvorljivost, dvojni električni sloj*

UVOD

Naziv minerala kalcita potiče od grčke reči *cals* koja označava gašeni kreč. Po hemijskom sastavu je $CaCO_3$, tvrdine po Mos-u 3 i vrlo je krt. Gustina čistog minerala je 2,72 kgm⁻³, a ako sadrži primese gustina varira od 2,7 kgm⁻³ do 2,85 kgm⁻³. Sjajnost mu je staklasta, a po ravnima cepljivosti može da se zapazi prelivanje boja. Kalcit je providan do mutan. Kada je čist i potpuno bezbojan naziva se islandski kalcit. Obično je beo, ali može biti i različito obojen: plavičast, sivkast, žut, zelenkast, crvenkast itd. Kalcit je relativno lako rastvoran pri delovanju atmosferskih padavina i površinskih voda pri čemu se prevodi u kalcijum - bikarbonat $Ca(HCO_3)_2$, koji je znatno rastvorljiviji od samog kalcijum karbonata [1].

Kalcit kristališe romboedarski. U prirodi se sreće veliki broj kristalnih formi (oko 300). Kristali su obično oblika prizme, romboedra ili skalenoedra, koji su najčešći. U nekim slučajevima nastajanja kalcita obrazuju se skeletni kristali. Javlja se u obliku stalaktita, zatim kao krupno do sitnozrnasti i kompaktni kalcit [1].

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EKSPERIMENTALNI DEO

Materijal i metode

Uzorak krečnjaka korišćen u eksperimentalnim ispitivanjima je iz ležišta „Venčac" - Aranđelovac. Karakterizacijom ovog uzorka utvrđeno da je dominantni mineral kalcit (> 95 %), pa će se u diskusiji rezultata umesto termina krečnjak koristiti termin kalcit. Za dobijanje kisele sredine korišćena je stearinska kiselina, $CH_3(CH_2)_{16}COOH$, tehničke čistoće, koju proizvodi firma „Fluka"-Švajcarska. Za rastvaranje kiseline upotrebljen je hloroform $CHCl_3$, p.a>99%, proizvođač „Centrohem" - Stara Pazova.

Postupak pripreme suspenzije za ispitivanje. U 500 ml destilovane vode zagrejane do 50^oC (temperatura merena termometrom), uz intenzivno mešanje, dodato je 50 g uzorka krečnjaka (kalcita) pri čemu je dobijena 9,1% suspenzija. Masa stearinske kiseline u 6 ovakvih proba obračunata na 100 g kalcita bila je: 0,5 g; 1 g; 1,5 g; 2 g; 3 g i 4 g. Pošto je stearinska kiselina dodavana u 100 g kalcita njena koncentracija je izražena u phr jedinicama (phr - Abbreviation for parts per hundred parts of resin). Vreme mešanja suspenzije je bilo 15 minuta, pri broju obrtaja na mešalici od 1500 ^{o}/min.

Postupak određivanje Ca^{2+} jona u vodenoj suspenziji kalcita. U 50 ml vode zagrejane na 50^oC dodato je 5 g kalcita i mešano na mešalici 1 min, a zatim je suspenzija centrifugirana. U dobijenom filtratu su određeni Ca^{2+} joni.

Za mešanje suspenzije je korišćena laboratorijska mešalica model „RE 166" proizvođača „Janke & Kunkel" - Nemačka, koja ima opseg 50 do 6000 ^{o}/min. Hemijski sastav krečnjaka i sadržaj Ca^{2+} jona u filtratu iz suspenzije je određen na atomskom apsorpcionom spektrofotometru tipa „Perkin Elmer 703 Analyst 300".

REZULTATI I DISKUSIJA

Hemijski sastav polaznog uzorka krečnjaka

Na osnovu sadržaja CaO koji je dobijen hemijskom analizom uzorka krečnjaka (54,77 %) i uz pretpostavku da je sav prisutan MgO (0,79 %) vezan za dolomit, računskim putem je dobijeno da u uzorku ima 95,84 % $CaCO_3$. Prema podeli krečnjaka, polazni uzorak spada u čist krečnjak, jer sadrži više od 95 % $CaCO_3$, a manje od 1,2 % MgO, [2].

Reakcije kalcita u vodenim rastvorima

Za definisanje sastava zasićenog vodenog rastvora kalcita neophodno je uzeti u obzir tri grupe ravnotežnih hemijskih reakcija [3]. Te reakcije su:

1. Ravnotežne hemijske reakcije karbonatnih vrsta u suspenziji kalcita i vode

$$(g) + \qquad \rightleftarrows \qquad (1)$$
$$\rightleftarrows \quad + \qquad (2)$$
$$\rightleftarrows \quad + \qquad (3)$$
$$+ \qquad (4)$$
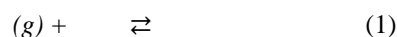
2. Ravnoteža jonskih parova

$$+ \qquad \rightleftarrows \qquad (5)$$

$$(6)$$
$$\rightleftarrows \qquad (7)$$

3. Ravnoteža čvrsto-tečno

$$(8)$$

Sastav zasićenog rastvora kalcita može biti otvoren ili zatvoren prema atmosferi. U otvorenom sistemu rastvor je uravnotežen sa parcijalnim pritiskom CO_2, $p(CO_2)$, jednačina 1, dok u zatvorenom sistemu nema razmene CO_2 sa atmosferom. pH rastvora može da se menja dodatkom kiselina ili baza kao i promenom $p(CO_2)$.

Distribucija jona i molekula u zatvorenom i otvorenom sistemu kalcit/voda

Distribucije jona i molekula koji se javljaju u zatvorenom i otvorenom sistemu kalcit/voda kao i distribucija hemijskih vrsta zasićenog vodenog rastvora kalcita u ravnoteži sa atmosferskim CO_2 $(p(CO_2) = 1,36 \times 10^{-4}$ bar), na 25°C prikazani su na slikama 1a, 1b i 1c [4]. Uočava se da na distribuciju hemijskih vrsta veliki uticaj ima pH i $p(CO_2)$ kao i međusobne reakcije hemijskih vrsta. Zavisnost udela hemijskih vrsta zasićenog vodenog rastvora kalcita od $p(CO_2)$ u zatvorenom i otvorenom sistemu prema atmosferi prikazana je na slikam 1a i 1b. Na slici 1b je prikazana distribucija hemijskih vrsta zasićenog vodenog rastvora kalcita u ravnoteži sa atmosferskim p(CO_2).

a) *b)*

c)
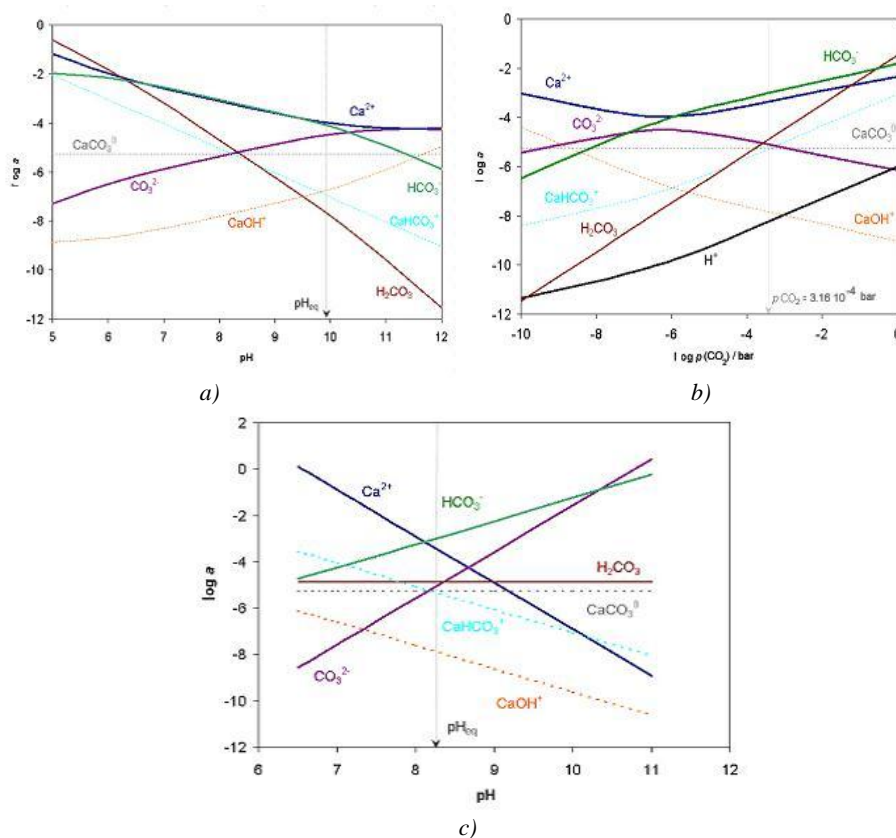
Sl. 1. *Distribucija jona i molekula zasićenog vodenog rastvora kalcita u zatvorenom (a) i otvorenom (b) sistemu kalcit/voda i distribucija hemijskih vrsta zasićenog vodenog rastvora kalcita u ravnoteži sa atmosferskim CO_2 $(p(CO_2)=1,36 \cdot 10^{-4}$ bar), na 25°C*

Na dijagramima prikazanim na slici 1a uočava se da sa povećanjem pH rastvora smanjuje udeo   i   jona, a povećava udeo   jona. Pri ravnotežnom pH (pH=9,9) u suspenziji dominiraju   i   dok su joni   prisutni u manjoj meri. Na dijagramima prikazanim na slici 1b uočava se da smanjenjem $p(CO_2)$ povećava

se pH rastvora kao posledica smanjenja koncentracije karbonatne kiseline. Pri smanjenju $p(CO_2)$ od 1,0 na 1,58·10^{-7} bar, ravnotežni pH se poveća od 6,0 do 11,3. Pri pH<10,5 u rastvoru dominiraju   i   joni, dok je   jon prisutan u manjoj meri. Kada pH poraste sa 6 na 10,5 ravnotežna koncentracija se   se povećava uz istovremeno smanjenje koncentracije   i   ali koji su i dalje dominantni u suspenziji. Pri pH>10,5 počinje dominacija   jona uz povećanje   jona kako bi se zadržala ravnoteža naelektrisanja. Sa dijagrama prikazanog na slici 1c vidi se da aktivnost   ne zavisi od pH i definisan je prema reakciji (1). U otvorenom sistemu pri konstantnom pCO_2 ($p(CO_2)$=1,36x10^{-4} bar) dodavanjem kiseline/baze (npr. HCl/NaOH) dolazi do promene pH rastvora. Dodatkom baze dolazi do povećanja koncentracije negativno naelektrisanih jona, uglavnom   i   , dok dodatak kiseline povećava koncentraciju pozitivno naelektrisanih jona, uglavnom   .

Međupovršina kalcit-voda

Mnogi istraživači si se bavili međupovršinom kalcit-voda. Tako je Hansen sa saradnicima [5] zaključio da se u prisustvu vode na površini kalcita odigrava reakcija prema sledećoj jednačini:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^-$$
(9)
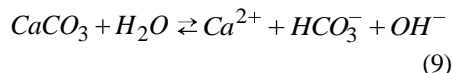
Kao rezultat ovog procesa suspenzija kalcita postaje alkalna. Koristeći rezultate Foxall-a i saradnika [6] ovi autori su istakli da kod kalcita, joni koji određuju elektrokinetičke osobine su joni kalcijuma i karbonatni joni, a ne H$^+$ i OH$^-$ joni. Ovi joni, odnosno pH sredine, određuju samo koja hemijska vrsta dominira u rastvoru: CO_3^{2-},   ili H_2CO_3. Određivanjem prisustva Ca^{2+} jona u vodenoj suspenziji kalcita koji je korišćen u ispitivanjima prikazanim u ovom radu dobijeno je 12 mg Ca^{2+}/litru. Prema nekim literaturnim podacima u kontaktu kalcita sa vodom formira se dvojni električni sloj prikazan na slici 2 [7].
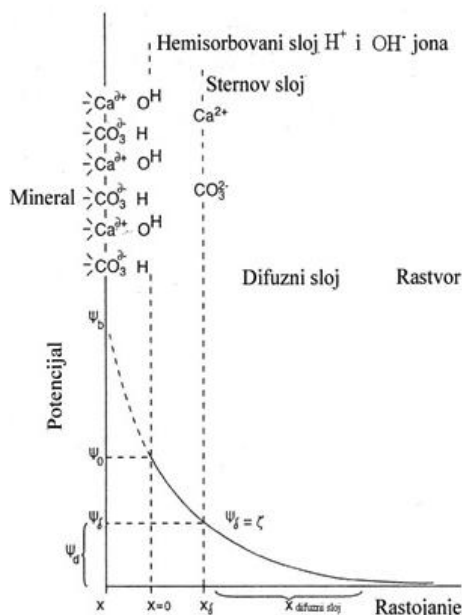
Sl. 2. *Model dvojnog električnog sloja kalcita na granici mineral/voda [7]*

Po ovom modelu dvojnog električnog sloja u kontaktu kalcita sa vodom neposredno uz graničnu površinu minerala, koju čine Ca^{2+} i CO_3^{2-} joni, nalaze se usled reakcije hidrolize hemisorbovani H^+ i OH^- joni. Ovi joni kompenzuju višak pozitivnog, odnosno negativnog naelektrisanja na površini kalcita. Uz nastali hemisorbovan sloj se u Šternovom sloju nalaze i adsorbovani joni kalcijuma i CO_3^{2-} joni. Upravo ovi joni su odgovorni za elektrokinetičke osobine minerala kalcita. Kada se hemisorbovan sloj H^+ i OH^- jona ukloni tada Ca^{2+} i CO_3^{2-} joni iz Šternovog sloja postaju ponovo sastavni deo trodimenzione kristalne rešetke kalcita.

Ispitivanja prikazana u ovom radu su pokazala da je kalcit mineral tipa soli i rastvorljiv u vodi. U nastaloj vodenoj suspenziji mogu se odigrati određene reakcije i formirati različiti joni i molekuli ugljene kiseline čija koncentracija zavisi od koncentracije rastvorenog CO_2 i pH rastvora (slike 1a, 1b, 1c). Iz rezultata koji si prikazani u ovom radu 9,1 % suspenzija polaznog uzorka kalcita specifične površine 4,8 m^2/g imala je pH=10,14 (slika 3.). Na osnovu alkalne vrednosti pH suspenzije zaključeno je da dominiraju reakcije koje su dovele do povećanja koncentracije hidroksilnih jona u rastvoru, kao npr. reakcija 10:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^-$$
(10).
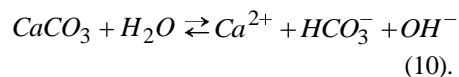
Na granici kalcit/voda formira se dvojni električni sloj, čija struktura, odnosno hidrofilne osobine minerala, zavise od koncentracije potencijalodređujućih jona, Ca^{2+} i CO_3^{2-}, rastvorenog CO_2 i pH rastvora (koncentracije jona H^+ i OH^-) i adsorpcije formiranih jona (i molekula) u rastvoru, koji su prema distribucionom dijagramu (slika 1a, 1b, 1c) dominantni u alkalnoj sredini. Struktura tako formiranog dvojnog električnog sloja dalje utiče i na interakciju minerala sa površinski aktivnom materijom (stearatnim jonom i molekulom stearinske kiseline), koja treba da dovede do hidrofobizacije mineralne površine.
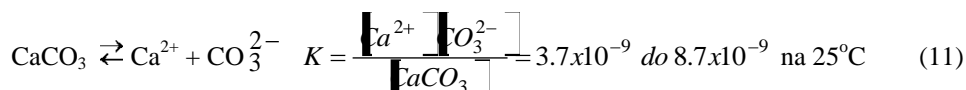
Reakcije kalcita u kiselom rastvoru

Prema literaturi adsorpcija stearinske kiseline na prirodnom kalcitu se obično odigrava u nepolarnom rastvaraču, jer se kalcit rastvara u vodi, a pH vodene sredine utiče kako na njegovu rastvorljivost tako i na stepen disocijacije stearinske kiseline. Međutim, Hansen i saradnici su ukazali da tretman kalcita sa vodom pre dodavanja rastvora stearinske kiseline u n-dekanu poboljšava adsorpciju stearinske kiseline na površini kalcita [5]. Kako bi se pratilo ponašanje kalcita u prisustvu stearinske kiseline dodavane su različite koncentracije stearinske kiseline i meren je pH svakog rastvora posle odvajanja čvrste faze. Dobijeni rezultati su upoređeni sa pH vrednosti 9,1 % suspenzije kalcita koja iznosi 10,14. Kriva zavisnosti pH rastvora od koncentracije dodate stearinske kiseline prikazana je na slici 3.
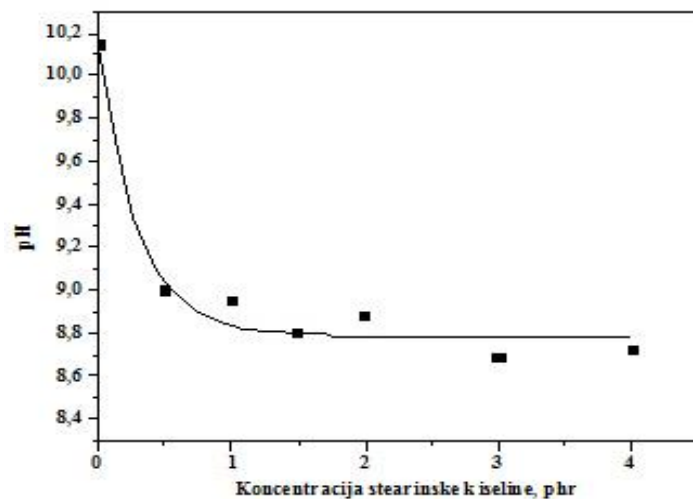
Sl. 3. *pH rastvora u zavisnosti od koncentracije stearinske kiseline*

Može se videti da pH 9,1 % vodene suspenzije kalcita iznosi 10,14 i da u prisustvu male koncentracije stearinske kiseline (0,5 phr ≈ 0,5 %) dolazi do opadanja pH vrednosti rastvora na pH = 9,00. Sa daljim povećanjem koncentracije stearinske kiseline zapaža se dodatno slabo opadanje pH vrednosti (pri koncentraciji stearinske kiseline od 1 phr pH iznosi 8,95, a pri koncentraciji od 4 phr ≈ 3,9 %, pH je 8,72). Osobine kalcijum karbonata u vodenom rastvoru su ispitivali mnogi istraživači [8]. Konstanta disocijacije kalcita na 25°C je reda veličine 10^{-9} i odvoja se prema reakciji 11.

$$\text{CaCO}_3 \rightleftarrows \text{Ca}^{2+} + \text{CO}_3^{2-} \quad K = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_3]} = 3.7x10^{-9} \; do \; 8.7x10^{-9} \; \text{na} \; 25^\text{o}\text{C} \qquad (11)$$

Suspenzija kalcit/H₂O ima prema nekim publikovanim podacima pH oko 9 [9], zavisno od parcijalnog pritiska CO₂. U vodenoj suspenziji kalcita se mogu prema reakcijama 1-8 javiti različiti joni i molekuli ugljene kiseline, čija koncentracija zavisi od koncentracije rastvorenog CO₂ i pH rastvora. Na osnovu prikazanih literaturnih podataka može se pretpostaviti da se i na granici kalcit/voda u 9,1 % suspenziji koja je korišćena u ovim ispitivanjima takođe formira dvojni električni sloj, ali u kome dominiraju joni koji su prema distribucionom dijagramu na pH=10,14 prisutni u datom sistemu.

Kako 9,1% suspenzije kalcita ima pH=10,14 (slika 3.), dakle veći od pKa stearinske kiseline (pKa = 5,7), nakon dodatka u ovu suspenziju rastvora stearinske kiseline u nepolarnom rastvaraču odigrava se i njena disocijacija:

$$\text{CH}_3(\text{CH}_2)_{16}\text{COOH} \; \rightleftarrows \; \text{CH}_3(\text{CH}_2)_{16}\text{COO}^- + \text{H}^+ \qquad (12)$$
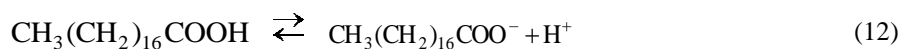
Kao posledica disocijacije stearinske kiseline raste koncentracija kako H^+ jona, tako i koncentracija $CH_3(CH_2)_{16}COO^-$, stearatnog jona (St^-). Rezultati u ovom radu to i potvrđuju s obzirom da dolazi do opadanja pH vrednosti rastvora nakon dodavanja i male koncentracije stearinske kiseline od 0,5 % (pH=9,00), odnosno do odigravanja reakcije neutralizacije.

Izoelektrična tačka (pH pri kome je zeta potencijal 0) se kod nekih uzoraka kalcita nalazi na pH= 11,4. Anjonski surfaktanti (površinski aktivne materije) se mogu više adsorbovati iz rastvora sa nižim pH vrednostima, međutim u kiseloj sredini $CaCO_3$ se raspada uz stvaranje CO_2, vode i jona Ca^{2+}. Prema Martinez-Luevanos-u i saradnicima [10], reakcija između $CaCO_3$ i protona se odigrava pri pH 8,3, tako da se do pH 8 ostvaruje najbolji balans između ove dve reakcije. Rezultati dobijeni u ovom radu su pokazali da u prisustvu stearinske kiseline pH suspenzije opada (slika 3). Pri koncentraciji 0,5 phr ≈ 0,5 % vrednost pH suspenzije je bila 9,00, dok je pri koncentraciji 4 phr iznosila 8,72. S obzirom da je pKa stearinske kiseline (pKa = 5,7) manji od pH 9,1 % suspenzije kalcita (pH=10,14), opadanje pH vrednosti se može objasniti, kako je već rečeno, disocijacijom stearinske kiseline u alkalnoj sredini reakcijom neutralizacije.

ZAKLJUČAK

Za ispitivanje reakcija kalcita u vodi korišćena je 9,1% suspenzija čiji je pH bio 10,14. Za ispitivanje reakcija u kiseloj sredini korišćena je tačno odmerena masa stearinske kiseline 0,5 g; 1 g; 1,5 g; 2 g; 3 g i 4 g dodate na 100 g kalcita. Rastvorljivost kalcita u vodi zavisi od rastvorenog CO_2 i pH sredine. Suspenzija kalcita koja je korišćena u ovim ispitivanjima imala je pH=10,14. Na osnovu alkalne pH vrednosti suspenzije moglo se zaključiti da u suspen-

ziji dominiraju reakcije koje dovode do povećanja koncentracije hidroksilnih jona, kao npr. reakcija: $CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^-$. Na granici kalcit/voda formirao se dvojni električni sloj. Njegova struktura, odnosno hidrofilne osobine, su zavisile od koncentracije potencijal određujućih jona, Ca^{2+} i CO_3^{2-}, pH sredine i adsorpcije molekula vode i jona (i molekula) formiranih u ovoj suspenziji usled njegove rastvorljivosti. Struktura tako formiranog dvojnog električnog sloja dalje je uticala na interakciju minerala sa površinski aktivnom materijom (stearatnim jonom i molekulom stearinske kiseline). U prisustvu stearinske kiseline pH vrednost suspenzije je opadala. Pri koncentraciji 0,5 phr vrednost pH je bila 9,00, a pri 4 phr 8,72. Imajući u vidu da je pKa stearinske kiseline (pKa = 5,7) manji od pH suspenzije kalcita (pH=10,14), opadanje pH vrednosti se objašnjava disocijacijom stearinske kiseline u alkalnoj sredini i reakcijom neutralizacije. Kao posledica disocijacije stearinske kiseline i reakcije neutralizacije u suspenziji su se pored nedisosovanih molekula kiseline nalazili u određenoj koncentraciji i stearatni joni $CH_3(CH_2)_{16}COO^-$, (St^-) koji su reagovali sa površinom minerala prevodeći je iz hidrofilne u hidrofobnu.

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