

An Adaptation Method for Removing Arsenate Species from Water Solution

Sainyam Galhotra¹, Shigeru Kanemitsu², Hiroyuki Kondo³

¹Xerox Research Center India, Bangalore

²Dept. of Information, Kinki University, Fukuoka, Japan

³Faculty of Environ. Chemistry, Fukuoka Women's University, Fukuoka, Japan

Email address:

sainyam.galhotra@xerox.com (S. Galhotra), kanemitu@fuk.kindai.ac.jp (S. Kanemitsu), kondo1808@fwu.ac.jp (H. Kondo)

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Abstract: This paper is based on the idea of adaptation under which we mean the replacement of one element in a system with another with similar aspects. The first adaptation comes from the replacement of orthophosphoric acid H_3PO_4 by arsenious acid H_3AsO_4 . There is a close relation between calcium-sulfate and calcium carbonate-arsenate species. The main objective of this note is to give an explicit formula for the ratio of each arsenal species to the total and to make an adaptation of the former by the latter to develop a new adsorption material of arsenic acid which spends almost no energy. Some recently proposed methods of using calcium sulphate or other material has ambivalent aspects regarding energy spending as well as the treatment after adsorption.

Keywords: Arsenate, Adsorption, Acidity (pH), Water Treatment

1. Introduction

The problem we are facing in the 21st century is decidedly that of getting as much as energy without giving too much burden on the environment. This problem, however, has been unnoticed, or noticed but neglected, by rapidly developing countries which want to attain swift industrial success. This is the track that we have once gone along and we know what will come. Thus, energy and environmental protection are the two sides of a coin and cannot be separated.

In this paper, as a manifestation of the principle of environmental protection with little energy, we shall consider the adsorption of arsenious acid by calcium carbonate.

Arsenic compounds contained in underground water are highly poisonous and when used as drinking water, it leads to possible damaging of health including blackfoot disease. There are many significant health damages reported in Bangladesh and India, especially in West Bengal area, as well as the wide area underground water pollution by arsenic compounds in southern area of Fukuoka Prefecture, Japan, revealed in 1994, most of which are due to natural causes.

The ionic characteristics of arsenic compounds is associated to that of the sodium carbonate and calcium

carbonate and higher concentration of arsenic compounds can be seen in deep sodium carbonate type underground water.

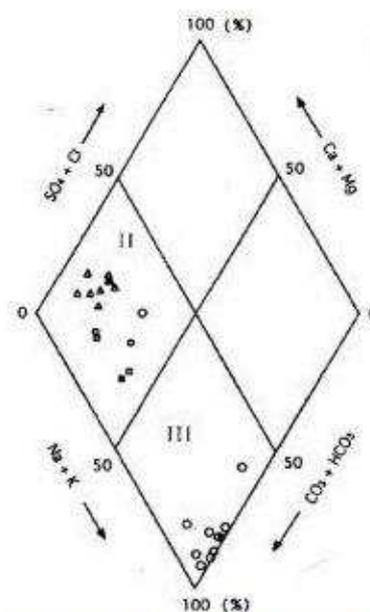


Fig. 1. Key Diagram of As contained in ground waters (n = 25)

In Fig. I, region II shows Calcium carbonate type ($n = 14$, As average $0.023\text{mg}/\ell$) while Region III shows sodium carbonate type ($n = 14$, As average $0.075\text{mg}/\ell$).

There is a long history of inhibition, by calcium adsorption, of eutrophication of waters, resulting from too much phosphate whose main ingredient is orthophosphoric acid H_3PO_4 . The third author in his thesis [6] took up the problem of removal of arsenious acid H_3AsO_4 by calcium adsorption. Our study as well as his is based on the principle of adaptation to the effect that chemical elements of similar structures and nature may be exchanged, yielding similar results and analysis can be done in much the same way.

In his thesis, he made a series of extensive experiments on calcium adsorption of arsenic acid on the adaption principle, i.e. substituting arsenic acid for orthophosphoric acid. There were several candidates for adsorption material including coral lime stone, activated alumina and calcium carbonate. He used three types of granules of oyster shells all of size smaller than 1mm: Type I are natural oyster shells, Type II and III are those which are calcined at 600°C for 2 hours with Type II in pelleted. Experiments were made with As water solution of 20 ml with As concentration $50\ \mu\text{g}/\text{ml}$. By his thorough investigation, it has been revealed that calcined oyster shells II, III showed 84.6 percent rate of adsorption, almost equal to that of activated alumina. This rate improved for higher concentration of As at concentration $10\sim 2000\ \text{g}/\text{ml}$. Type I shells showed 17~37 percent adsorption rate for the use of more than 0.5g and 2g the rate was the highest.

The pH value of the resulting water solution was 8.1~9.0 for Type I while it was 9.8~10.7 for Type II and III, surpassing the tap water limit of 5.8~8.6. The third author conjectured that the reason for better adsorption due to the fact that by calcination, calcium carbonate changes into water-soluble calcium oxide CaO (quicklime). He confirmed his conjecture by using the neutralized Type II shells which showed weaker adsorption efficiency. It has been verified that Type II, III shells are very effective in adsorption but have the defect of producing strong alkali solution.

Recently there appeared a paper [10] which proposes the use of calcium sulfate (gypsum) CaSO_4 as adsorption material for arsenious acid. This lies at the opposite end of the spectrum of adsorption, yielding strong acidity in addition to sulphur although it has a far stronger in adsorbing power than calcium carbonate.

The same problem occurs with oyster shells which liquate out heavy metal ions contained in them, including Cr, Sr, Mo from calcined ones and Sr, Mo, Mn from Type I, causing a plausible secondary pollution.

Calcined calcium carbonate (quicklime), as adsorption material, suffers from two defects, i.e. it is strong alkali and needs to be burnt at the temperature of $900^\circ\sim 1500^\circ$. Shell lime is made by calcination at 300° while the building material is made at 1500° , which gives rise to mortar.

It seems that adsorption of As and liquation of ingredients are in ambivalent balance and we should choose the most

economical Type I shells since they are industrial wastes.

Thus Type I shells may be worth further being studied as to why they show the most effective rate for 2g for water solution 20ml of As concentration $50\ \mu\text{g}/\text{ml}$ and why the rate decreases thereafter. The third author conjectures that this might be caused by the rising of pH of the solution.

There are subtleties of dissociation of which family of acids are prevailing according to the proton index. We restrict to the range 5.8~8.6 which is allowed as tap water in Japan. Our purpose is to make clear the underlying chemical structure by mathematical reasoning.

This paper is a starter for extensive research on the adaptation principle. The optimal choice of the adsorption material according to higher concentration of As or its equivalent is conducted elsewhere.

2. Adaption Principle

Let X denote one of SO_4^{2-} , HCO_3^- , CO_3^{2-} and F_2^- . Their compound with calcium ion CaSO_4 , $\text{Ca}(\text{HCO}_3)_2$, CaCO_3 and CaF_2 are calcium sulfate, calcium hydro-carbonate, calcium carbonate, calcium fluoride, respectively, referred to above. The well-known formula for the solubility product reads

$$K_{s,\text{Ca}X} = [\text{Ca}^{2+}][X^{2-}] \quad (1)$$

and for $X = \text{SO}_4$, Eq. (1) reads

$$K_{s,\text{CaSO}_4} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 2.4 \times 10^{-5} \text{mol}^2 \text{dm}^{-6}, \quad (2)$$

for HCO_3^-

$$K_{s,\text{CaH}(\text{CO}_3)_2} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 = 1.02 \text{mol}^3 \text{dm}^{-9}, \quad (3)$$

and for $X = \text{CO}_3^{2-}$

$$K_{s,\text{CaCO}_3} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 4.8 \times 10^{-9} \text{mol}^2 \text{dm}^{-6}. \quad (4)$$

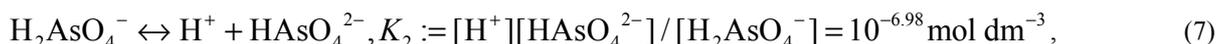
We notice the principle to the effect that the smaller the exponent a of 10^a is, the less soluble the material is, i.e. the more precipitative. In the above case, CaSO_4 is more soluble than CaCO_3 .

On the other hand, the solubility product formula for the calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$ is

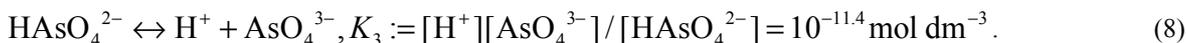
$$K_{s,\text{Ca}_3(\text{AsO}_4)_2} = [\text{Ca}^{2+}]^3[\text{AsO}_4^{3-}]^2 = 6.8 \times 10^{-19} \text{mol}^5 \text{dm}^{-15}. \quad (5)$$

By the above principle, calcium arsenate is much less soluble than calcium sulfate and calcium carbonate, i.e. in the presence of the latter, the arsenate ions AsO_4^{3-} precipitate, thereby adsorption being done. They arise by the dissociation of the protons from arsenic acid in the following successive dissociation equilibrium.





and



Let A_{S_T} denote the total concentration of all arsenic species:

$$A_{S_T} = [\text{H}_3\text{AsO}_4] + [\text{H}_2\text{AsO}_4^-] + [\text{HAsO}_4^{2-}] + [\text{AsO}_4^{3-}] \quad (9)$$

and let α_j denote the ratio of each arsenic species against the total:

$$\alpha_3 = [\text{AsO}_4^{3-}] / A_{S_T} \quad (11)$$

$$\alpha_j = [\text{H}_{3-j}\text{AsO}_4^{j-}] / A_{S_T}, \quad 0 \leq j \leq 3, \quad (10)$$

will play the important role.
Noting that Eq. 6, Eq. 7, Eq. 8 may be unified into

where $\alpha_0 = [\text{H}_3\text{AsO}_4]/A_{S_T}$ and

$$K_j = [\text{H}^+][\text{H}_{3-j}\text{AsO}_4^{j-}] / [\text{H}_{4-j}\text{AsO}_4^{(j-1)-}] = [\text{H}^+] \frac{[\text{H}_{3-j}\text{AsO}_4^{j-}] / A_{S_T}}{[\text{H}_{4-j}\text{AsO}_4^{(j-1)-}] / A_{S_T}} = [\text{H}^+] \frac{\alpha_j}{\alpha_{j-1}}, \quad 1 \leq j \leq 3, \quad (12)$$

we obtain by Eq. 12

$$\alpha_j = K_j [\text{H}^+]^{-1} \alpha_{j-1}, \quad 1 \leq j \leq 3, \quad (13)$$

the relation between successive terms of the sequence, whence inductively we conclude that

$$\alpha_j = K_j \cdots K_1 [\text{H}^+]^{-j} \alpha_0, \quad 1 \leq j \leq 3. \quad (14)$$

Recall that the sum of α_j 's is 1 by Eq. 10

$$\sum_{j=1}^3 \alpha_j = 1. \quad (15)$$

Substituting from Eq. 14 we conclude that

$$\alpha_0 = \frac{1}{1 + \sum_{i=1}^3 K_i \cdots K_1 [\text{H}^+]^{-i}}. \quad (16)$$

Hence from Eq. 14 and Eq. 16 we obtain
Theorem 1: We have the explicit formula

$$\alpha_j = \alpha_j([\text{H}^+]) = \frac{K_j \cdots K_1 [\text{H}^+]^{-j}}{1 + \sum_{i=1}^3 K_i \cdots K_1 [\text{H}^+]^{-i}}, \quad 1 \leq j \leq 3. \quad (17)$$

Or more concretely,

$$\alpha_j = \alpha_j([\text{H}^+]) = \frac{K_j \cdots K_1 [\text{H}^+]^{3-j}}{[\text{H}^+]^3 + 10^{-2.22}[\text{H}^+]^2 + 10^{-9.2}[\text{H}^+] + 10^{-20.6}}. \quad (18)$$

Proof. Eq. 18 follows from the numerical values in Eq. 6, Eq. 7, Eq. 8

$$K_1 K_2 = 10^{-9.2}, \quad K_1 K_2 K_3 = 10^{-20.6} \quad (19)$$

and by multiplying by $([\text{H}^+])^3$ the numerator and the denominator of Eq. 17.

$$\text{E.g. } \alpha_2 = \alpha_2([\text{H}^+]) = \frac{10^{-9.2}[\text{H}^+]}{[\text{H}^+]^3 + 10^{-2.22}[\text{H}^+]^2 + 10^{-9.2}[\text{H}^+] + 10^{-20.6}}$$

and

$$\alpha_3 = \alpha_3([\text{H}^+]) = \frac{10^{-20.6}}{[\text{H}^+]^3 + 10^{-2.22}[\text{H}^+]^2 + 10^{-9.2}[\text{H}^+] + 10^{-20.6}}. \quad (20)$$

Eliminating $[Ca^{2+}]$ from Eq. 1 and Eq. 5, we obtain

$$\frac{K_{s, CaX}^3}{K_{s, Ca_3(AsO_4)_2}} = \frac{[X^{2-}]^3}{[\text{AsO}_4^{3-}]^2}. \quad (21)$$

From Eq. 11 we have

$$[\text{AsO}_4^{3-}] = \alpha_3 A_{S_T},$$

whence we deduce from Eq. 21 that

$$[X^{2-}] = R(\alpha_3 A_{S_T})^{2/3} \quad (22)$$

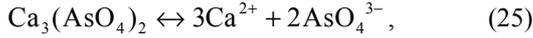
on writing

$$R = R_X = \frac{K_{s, CaX}}{(K_{s, Ca_3(AsO_4)_2})^{1/3}}. \quad (23)$$

In the case of $X = \text{HCO}_3^-$,

$$R_{\text{HCO}_3} = \frac{1.06 \text{ mol}^3 \text{ dm}^{-9}}{(6.8 \times 10^{-19} \text{ mol}^5 \text{ dm}^{-15})^{1/3}} = 0.546 \times 10^{-2} \text{ mol}^{1/3} \text{ dm}^{-1}. \quad (24)$$

From



we find that the concentration of As_T is approximately 3/2 of that of Ca_3 , whence we deduce the formula

$$[\text{Ca}^{2+}] = [X^{2-}] + \frac{3}{2} \text{As}_T \quad (26)$$

as in [10,11]. Then substituting Eq. 22 we obtain

$$[\text{Ca}^{2+}] = R_X (\alpha_3 \text{As}_T)^{2/3} + \frac{3}{2} \text{As}_T. \quad (27)$$

Substituting Eq. 22 and Eq. 27 in Eq. 1, we deduce that

$$K_{s,\text{CaX}} = R_X^2 \alpha_3^{4/3} \text{As}_T^{4/3} + \frac{3}{2} R_X \alpha_3^{2/3} \text{As}_T^{5/3} \quad (28)$$

and we are to solve the quintic equation with coefficients

containing the parameter $[\text{H}^+]$

$$\frac{3}{2} R_X \alpha_3^{2/3} P^5 + R_X^2 \alpha_3^{4/3} P^4 - K_{s,\text{CaX}} = 0 \quad (29)$$

on writing $P = \text{As}_T^{1/3}$. E.g. by the well-known Newton iterative method, the equation Eq. 29 may be solved numerically. We are to solve it with $X = \text{HCO}_3^-$ i.e. with the value in Eq. 24.

$$P^5 + \frac{2}{3} R_{\text{CO}_3} \alpha_3^{2/3} P^4 - \frac{2}{3} R_{\text{CO}_3}^{-1} \alpha_3^{-2/3} K_{s,\text{CaCO}_3} = 0 \quad (30)$$

with $\alpha_3 = \alpha_3([\text{H}^+])$ = defined by Eq. 20, Fig. 2 shows the graph of $P = \text{As}_T^{1/3}$.

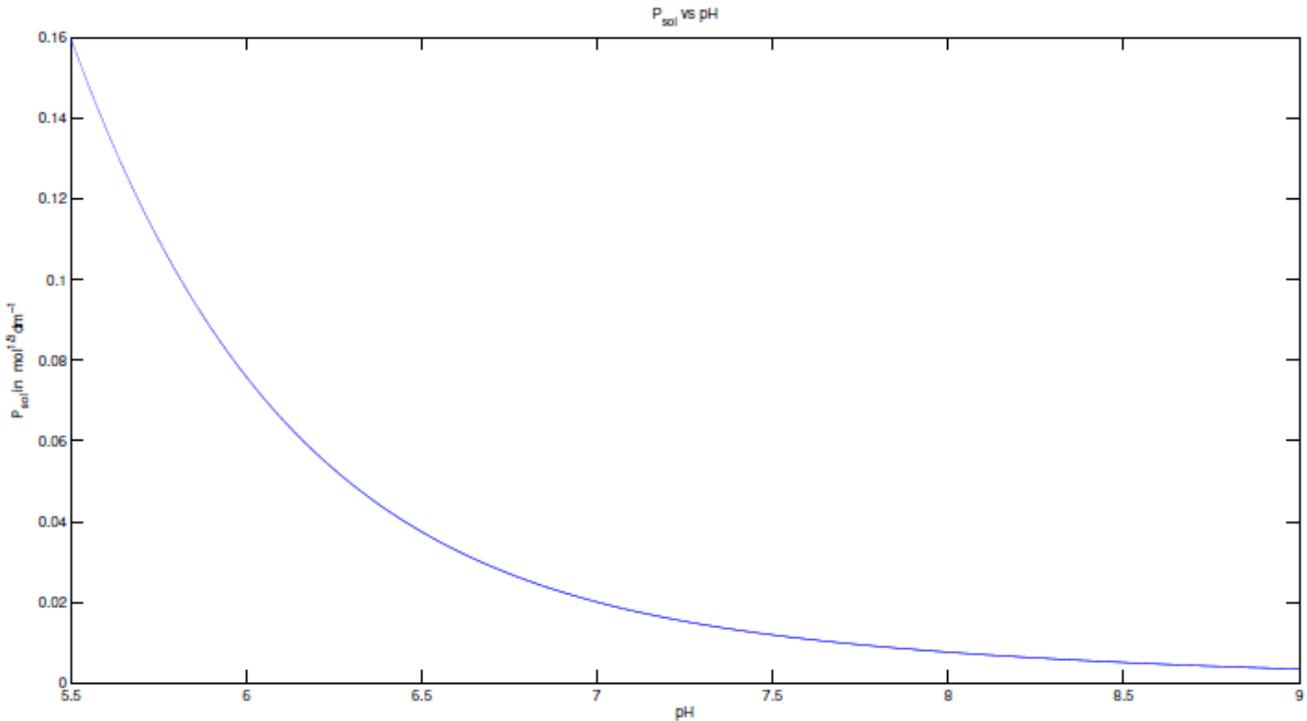


Fig. 2. The positive solution of the quantic equation for different values of pH between 5.5 and 8.5

Remark: The acidity of tap water is restricted to the range 5.8~8.6 by law and underground water has neutral or weak alkali and so the pH lies near and greater than 7. In [10] the pH range is restricted to 7~10 since $K_2 \approx 10^{-7}$, $\alpha_2 = 10^{-7}[\text{H}^+]^{-1}\alpha_1$ and for pH=7, we have $\alpha_2 = \alpha_1$ and as pH increases the proportion of H_2AsO_4^- against HAsO_4^{2-} steadily decreases. In [10] the argument goes in the following lines. HAsO_4^{2-} starts predominating $\text{H}_2\text{AsO}_4^{1-}$, so that one may approximate the

amount of HAsO_4^{2-} and so one may obtain the amount of As_T by solving the Eq. 28 with $X = \text{SO}_4^-$.

In the case of HCO_3^- , it predominates CO_3^{2-} at pH=8.3 by 100 times and only at pH =10.3, their amount becomes equal. Hence there are three ways to go. We assume the pH range to 5.8 ~ 8.3, which is more practical or we assume pH > 10.3 Or we calcite the lime stone to produce quicklime. We can make a table of temperature needed for the degree of adsorption.

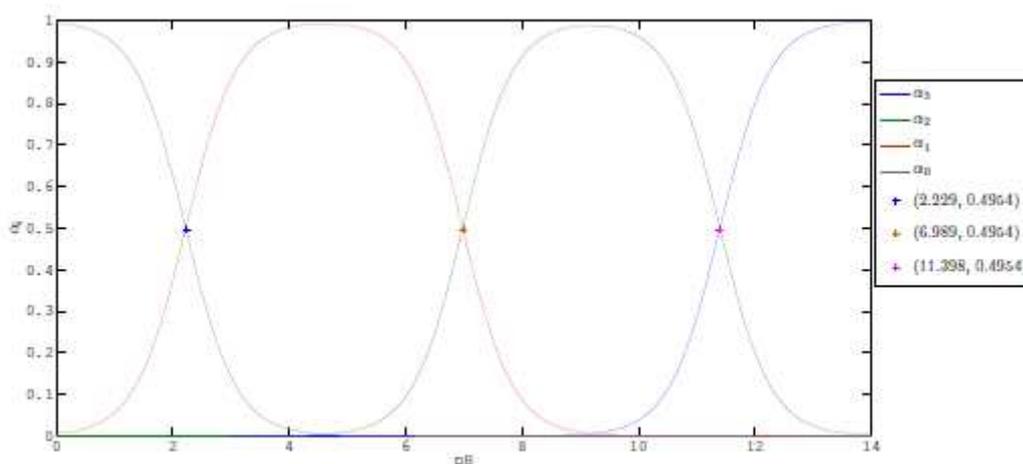


Fig. 3. $\alpha_{0,1,2,3}$ value for different values of pH

3. Calcium Phosphate

The solubility product formula Eq. 1 takes on another form according to the compound we consider. For the ease of detection, in progressive experiments, we have been trying to measure the amount of phosphate rather than arsenal, which should give as good detection result for the latter as the former, in view of the adaption principle referred to in Introduction. In this section we shall state the theoretical

values for the ratios as in II.

Theorem 2: Let

$$\beta_j = \frac{[H_{3-j}PO_4^{-j}]}{P_T} \tag{31}$$

Then Eq. 18 reads

$$\beta_j = \beta_j([H^+]) = \frac{K_j \dots K_1 [H^+]^{3-j}}{[H^+]^3 + 7.5 \times 10^{-3} [H^+]^2 + 4.65 \times 10^{-10} [H^+] + 9.95 \times 10^{-23}} \tag{32}$$

I.e.

$$\beta_1 = \beta_1([H^+]) = \frac{7.5 \times 10^{-3} [H^+]^2}{[H^+]^3 + 7.5 \times 10^{-3} [H^+]^2 + 4.65 \times 10^{-10} [H^+] + 9.95 \times 10^{-23}} \tag{33}$$

$$\beta_2 = \beta_2([H^+]) = \frac{4.65 \times 10^{-10} [H^+]}{[H^+]^3 + 7.5 \times 10^{-3} [H^+]^2 + 4.65 \times 10^{-10} [H^+] + 9.95 \times 10^{-23}} \tag{34}$$

and

$$\beta_3 = \beta_3([H^+]) = \frac{9.95 \times 10^{-23}}{[H^+]^3 + 7.5 \times 10^{-3} [H^+]^2 + 4.65 \times 10^{-10} [H^+] + 9.95 \times 10^{-23}} \tag{35}$$

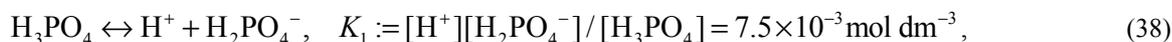
Proof: Corresponding to Eq. 25, we have

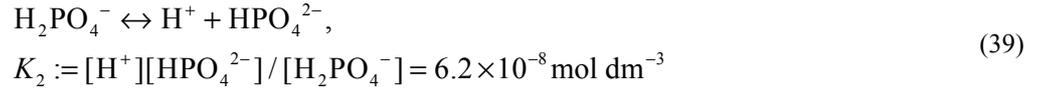


so that Eq. 1 reads

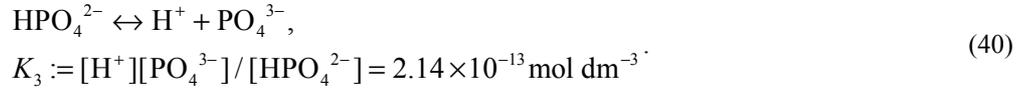
$$K_{s,Ca_3((PO)_4)_2} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 2.0 \times 10^{-29} \text{ mol}^5 \text{ dm}^{-15} \tag{37}$$

Eq. 7, 8, 9 read respectively





and



Now Eq. 19 takes the form

$$K_1 K_2 = 4.65 \times 10^{-10}, \quad K_1 K_2 K_3 = 9.95 \times 10^{-23}. \quad (41)$$

Incorporating these completes the proof.

Eq. 27 remains the same with As replaced by PO_4 and we are to solve the quintic equation corresponding to Eq. 29

$$\frac{3}{2} R_X \beta_3^{2/3} P^5 + R_X^2 \beta_3^{4/3} P^4 - K_{s,\text{CaX}} = 0. \quad (42)$$

on writing $P = ((\text{PO}_4)_T)^{1/3}$. We are to solve it with $X = \text{CO}_3$ i.e. with the value Eq. 24:

$$P^5 + \frac{2}{3} R_{\text{CO}_3} \beta_3^{2/3} P^4 - \frac{2}{3} R_{\text{CO}_3}^{-1} \beta_3^{-2/3} K_{s,\text{CaCO}_3} = 0 \quad (43)$$

with $\beta_3 = \beta_3[\text{H}^+]$ given by Eq. 35.

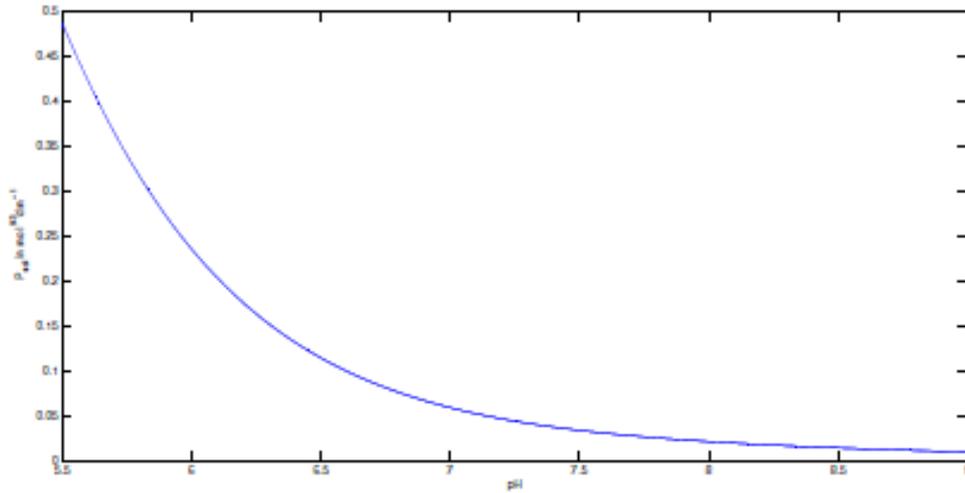


Fig. 4. The positive solution of the quintic equation for different values of pH between 5.5 and 9

Fig. 3 shows the graph of $P = ((\text{PO}_4)_T)^{1/3}$

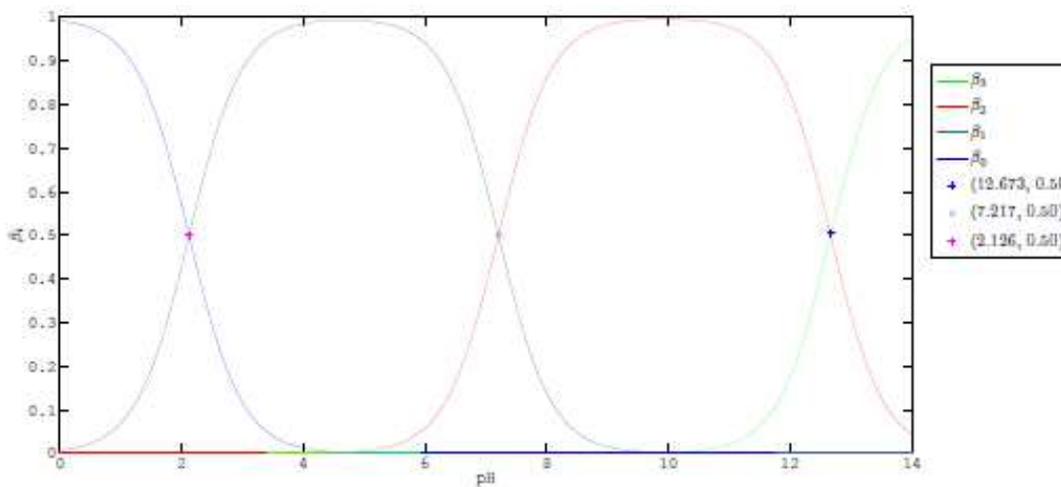


Fig. 5. $\beta_{0,1,2,3}$ value for different values of pH

4. Dissociation of Calcium Carbonate



Since calcium carbonate is a weak acid, there is a subtle problem As to which ionic species prevails at a specified range of pH. The following is a preliminary study on the dissociation equilibrium for calcium carbonate. First,

$$\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-, \quad k_2 = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]=10^{-6.3}, \tag{45}$$

$$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}, \quad k_3 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]=10^{-10.3}. \tag{46}$$

Along with eq. 10 we let

$$\gamma_j = [\text{H}_{2-j}\text{CO}_3^{j-}]/\text{CO}_T, \quad 0 \leq j \leq 2, \tag{47}$$

where CO_T indicates the total amount of CO. More concretely,

$$\gamma_0 = [\text{H}_2\text{CO}_3]/\text{CO}_T, \gamma_1 = [\text{HCO}_3^-]/\text{CO}_T, \gamma_2 = [\text{CO}_3^{2-}]/\text{CO}_T. \tag{48}$$

As with Theorem 1, we obtain

Theorem 3:

$$\gamma_1 = \frac{10^{-6.3}[\text{H}^+]^{-1}}{1 + 10^{-6.3}[\text{H}^+]^{-1} + 10^{-16.6}[\text{H}^+]^{-2}}, \quad \gamma_2 = \frac{10^{-16.6}[\text{H}^+]^{-2}}{1 + 10^{-6.3}[\text{H}^+]^{-1} + 10^{-16.6}[\text{H}^+]^{-2}}. \tag{49}$$

Proof: In analogy to Eq. 12 we sum up to get

$$k_{j+1} = [\text{H}^+] \frac{\gamma_j}{\gamma_{j-1}}, \quad 1 \leq j \leq 2. \tag{50}$$

Hence we obtain the relation between the consecutive terms

$$\gamma_j = k_{j+1}[\text{H}^+]^{-1} \gamma_{j-1}, \quad 1 \leq j \leq 2. \tag{51}$$

whence inductively,

$$\gamma_j = k_{j+1} \cdots k_2 [\text{H}^+]^{-j} \gamma_0, \quad 1 \leq j \leq 2, \tag{52}$$

$$\gamma_1 = k_2 [\text{H}^+]^{-1} \gamma_0, \quad \gamma_2 = k_3 k_2 [\text{H}^+]^{-2} \gamma_0. \tag{53}$$

Here we use $\gamma_0 + \gamma_1 + \gamma_2 = 1$ to deduce as we did Eq. 16,

$$\begin{aligned} \gamma_0 &= \frac{1}{1 + \sum_{i=2}^3 k_i \cdots k_2 [\text{H}^+]^{1-i}} = \frac{1}{1 + k_2 [\text{H}^+]^{-1} + k_2 k_3 [\text{H}^+]^{-2}} \\ &= \frac{1}{1 + 10^{-6.3} [\text{H}^+]^{-1} + 10^{-16.6} [\text{H}^+]^{-2}}. \end{aligned} \tag{54}$$

In the range 5.8 – 8.6 of pH which is a regulation by law, both exist in notable quantity. E.g. For pH =7, the rate CO_3^{2-} is

$$\gamma_2 = \frac{10^{-2.6}}{1 + 10^{0.7} + 10^{-2.6}} = \frac{1}{1 + 10^{3.3} + 10^{2.6}} \approx 4.110^{-4},$$

which is neglected in [9]. On p.v. of that paper, $10^{-5} \sim 10^{-2}$ is

which indicates the solution of carbon dioxide with water and which is irrelevant to us here. What may have to do with are the following:

regarded as negligible quantity.

5. Conclusion

As discussed, the main motive of this paper was to explore adaption principle i.e. replacing arsenate occurrences by other Ions like carbonate and phosphates. The main aim of developing this technique is to clean the water being supplied by removing poisonous arsenic occurrences and to use minimum amount of energy. The paper explores the use of oyster shells which are an industrial waste or the removal of arsenic. The analysis has shown that we can save on energy if we keep an optimum pH and replace the arsenate ions by phosphates or carbonates.

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