Desorption of Fe, Cu, Zn and Mn Metal Cations and Prevention of Phosphate Sorption by EDTA under Standard Metal-Calcite and Gypsum Systems

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ABSTRACT

The influence of EDTA on the P sorption prevention and Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} desorption, under standard calcite and gypsum systems were studied. Fixed levels (20 ppm of each) of Fe, Cu, Zn and Mn chlorides, were first reacted with fixed weight (2.5 g) of either calcite or gypsum for 24 hours. Then fixed levels of P (20 ppm) plus variable rates of EDTA were introduced to the previous solutions and reacted for 48 hours. The filtrate analysis showed that EDTA prevented 25 and 56% of the added P, at 0.1 and 3.0 mMO.C L^{-1} of EDTA, respectively under calcite system. Then a sudden sorption accompanied by a sudden pH rise took place at 5.0 and mMO.C L^{-1} of EDTA. However, under gypsum systems, the results were generally misleading, and the EDTA prevented 39.5% of the added P at the highest rate of it. Under calcite systems, EDTA failed to desorb Fe^{3+} at all rates, while it desorbed 59, 59.5 and 38.5% of Cu^{2+}, Zn^{2+} and Mn^{2+}, respectively at the highest rate of it. On the other hand, the metal desorption by EDTA under gypsum systems was misleading for all metals applied. However, under gypsum systems, the strongly significant sorption of Fe^{3+} in the control, as well as, at the lowest rates of EDTA, was attributed to a theoretically hypothesized precipitate, ($FeSO_4H_2PO_4$) which was suggested to form under low pH (pH = 4.5) conditions. Furthermore, the present study did not show significant calcite dissolution within the EDTA rates applied.

Key words: calcareous; gypsiferous; ligand exchange; organic anion sorption; desorption

INTRODUCTION

The importance of the organic chelating agents toward heavy metals sorption, desorption, solubility and the stability of their associated compounds under various soil conditions, has been the concern of many investigators (Lindsay et al., 1967; Lindsay and Norvell, 1969; Halvorson and Lindsay 1972; Lahar and Zipori, 1978; Cline et al., 1982; Elrashid and O'Conner, 1982; Norvell and Lindsay 1982; Asher and Yosef, 1982; Vulava et al, 1997; and Gwo and Jardine, 2005). It has been reported that metal chelation must be considered an important mechanism, which may influence the solubility and movement of metals in soils (Means et al., 1978 and Elsokkary, 1980). Krauskopf (1972) reported that Zn forms soluble complexes with organic ligands such as EDTA and DTPA. It was reported, however, that metal complexation by solution ligands can either enhance, inhibit or has no effect on metal adsorption mechanism, and such phenomenon was a function of many parameters, some of which, the type and amount of both metal and the complexing agent, in addition to the nature of the adsorbent surface.

However, the importance of these ligands that they are able to form complexes with heavy metals and such complexes were found to be more soluble than the free metal ions (Norvell, 1982). The effect of calcium concentration on the fixation of Fe-EDTA was reported quantitatively recently, through column technique design (Lahar, 1978) where he showed that in the three different soils tested, the increasing Ca^{2+} concentration decreased the recovery of Fe in the effluent. Lindsay et al. (1967), in their study of the development of stability – pH diagrams to predict the behavior of Fe chelates in soils where they employed the three synthetic chelating agents EDTA (ethylene diaminetetra acetic acid), DTPA (diethylene triamine penta acetic acid), and EDDHA [ethylene diamine di (o-hydroxyphenylacetic acid)] in which all the three chelates were saturated with Fe at low pH values reported, however, that as pH increased above 6, Fe^{3+} was displaced by Ca^{2+} to produce Ca $EDTA^{2-}$ and precipitated iron oxide, whereas above pH 7, Fe $DTPA^{-2}$ followed similar exchange, but Fe $EDDHA^{-}$ remained stable throughout the pH range of 4 to 10. They reported that such behavior was in close agreement with those reported under actual soil conditions. Vulava et al. (1997) reported that the order of application of Cu^{2+} and DTPA to soil also strongly influenced Cu solubility, and the highest solubility was attained when the DTPA was applied first and reacted with soil. They, however, attributed such results to the surface coordination of DTPA, which prevented Cu from binding with soils. They also reported that an increase in background electrolyte concentration was accompanied by a decrease in the pH value which resulted in a change in Cu^{2+} solubility. In general, the pH value, type and nature of the metal and the complexing agent, the relative and absolute concentrations of the metal or the complexing agents, the ionic strength of solution, the order of application of either the metal or ligand and finally the kind and nature of the solid phase surface sites, all of these factors have been reported to determine the nature of chemical sorption reactions and their resultant complexes (Elliott and Huang, 1980, 1979; Davis and Leckie, 1978; Vuceta and Morgan, 1978; Elliott and Huang, 1985; Basta and Tabatabi, 1992 a, b;

Bryce et al., 1994). In addition, Norvell and Lindsay (1969), reported that during the reaction of Mn EDTA with soils, Mn was displaced from the chelate complex by Fe at low pH values and by Ca at high pH values. They, however, attributed such behavior to the dissolution of Fe from soils under low pH values, which displaced Mn from the chelate and precipitating the released Mn in insoluble form.

Moreover, in addition to the role of the chelating agents concerning heavy metal chemistry in soils, and their variable influencė on their compound sorption, desorption and stability, as well as, their impact on different natural environmental aspects, one might think about their role concerning phosphate sorption prevention, under certain soil conditions. Under calcareous or gypsiferous soil conditions, where calcite or gypsum components would be present in meaningful amounts, would mostly control the nature of the chemical reactions under such environments. Heavy metals, as well as phosphate, would be expected to face an almost similar fate under such conditions. Heavy metal carbonates, hydroxides precipitate and metal surface sorption, in addition to phosphate sorption and insoluble Ca-phosphate minerals formed under calcareous soil conditions, have been reported by many investigators (Cole et al., 1953, Clark and Turner, 1954; Kuo and Lotse, 1972; and Al-Shabaan, 1989).

Due to the existence of calcareous and gypsiferrous soil conditions, under arid environments, one might be interested to compare the behavior of the important chelating agent (EDTA) toward the fixation problems, that face phosphate and heavy metals under such environments. The purpose of the present research was:

i) to test the effectiveness of the EDTA (ethylene diaminetetra acetic acid) toward Fe, Cu, Zn and Mn metal cations desorption, after they were sorbed on absolute standard calcite or gypsum surfaces.

ii) to test the EDTA effectiveness as well toward preventing phosphate sorption which was applied with the chelate, at the

iii) same time to the same standard calcite or gypsum media that sorbed the pre-mentioned metal cations.

MATERIALS AND METHODS

- The metal cations presorption stage.

Standard salt reagent grades of $FeCl_3$, $CuCl_2$, $ZnCl_2$ and $MnCl_2$ were chosen, as sources of Fe3+, Cu^{2+}, Zn^{2+} and Mn^{2+} metal cations. Stock solution of 200 ppm of each metal was prepared together in 0.02 M KCl background electrolyte matrix in one container. Five mls of the stock solution were added to 2.5g of calcite or gypsum (reagent grades), which were previously placed in 50 ml screw caps polyethylene centrifuge tubes. The tubes were held vertically on a proper holder with closed caps then shaken circularly on a proper shaker, at 140 rpm for 24 hours, after which the metal cations were assumed to be sorbed.

- The P sorption prevention and the presorbed metal cations release stage.

Several stock solutions of fixed P concentration (20 ppm) were prepared from the standard reagent of KH_2PO_4 in 0.02 M KCl electrolyte matrix plus, an appropriate level of either 0.0, 0.1, 0.3, 0.5, 0.7, 1.0, 3.0, 5.0, 7.0, 10.0 or 15.0 mML^{-1} of standard reagent of EDTA (ethylene diaminetetra acetic acid). Then forty five mls of each treatment stock were added to each of the three (triplication) tubes, which contained the presorbed metal cations under calcite or gypsum systems from the previous stage, so that the final total solution volume within each tube would be 50 mls, while each treatment was triplicated as well. The tubes were closed and arranged horizontally in proper holders, then shaken at 140 rpm for 48 hours on a proper shaker provided the lab temperature and pressure were at the standard conditions. At the end, the treatment solutions were properly centrifuged and filtrated through Watman 42 filter papers. The filtrates were analyzed for pH and EC, then for HCO^{-}_3 and/or Co^{2-}_3 (for calcite systems) by titration due to the method described in the Agriculture Handbook, No. 60, 1969. The Fe3+, Cu^{2+}, Zn^{2+} and Mn^{2+} and P were determined by an Inductively Coupled Plasma Optical Emission Spectro-Meter instrument (ICP).

Table 1: Shows the mean values of the triplicated treatments of the equilibrium electrical conductivities (EC), pH, bicarbonate, calcium, phosphate, Fe, Cu, Zn and Mn concentrations as functions of the increasing rate of the EDTA under calcite systems.

EDTA rate mML^{-1}	EC mmohs Cm^{-1}	pH	Ppm						
			HCO_3^-	Ca^{2+}	P	Fe	Cu	Zn	Mn
0.0	3.04	7.11	386	50.2	7.0	0.04	0.04	0.14	1.5
0.1	3.24	7.05	400	47.3	12.0	0.04	0.9	0.22	2.5
0.3	3.15	7.26	390	42.4	12.3	0.04	1.7	0.35	2.6
0.5	3.11	7.21	387	42.4	12.7	0.04	2.9	0.38	2.8
0.7	3.13	7.60	379	45.1	12.9	0.04	3.9	0.55	3.0
1.0	3.14	7.28	378	47.7	14.5	0.04	6.9	1.2	4.0
3.0	3.03	7.35	402	53.1	18.2	0.04	10.9	8.8	4.6
5.0	3.06	8.36	389	52.2	5.9	0.04	11.5	10.7	6.3
7.0	3.01	8.57	385	53.0	5.3	0.04	11.3	10.9	7.0
10.0	3.32	8.64	383	55.5	4.2	0.04	11.7	11.2	7.5
15.0	3.00	8.7	400	56.1	3.7	0.04	11.9	11.9	9.2

Table 2: Shows the mean values of the triplicated treatments of equilibrium phosphate, Fe, Cu, Zn, Ca and Mn concentrations as functions of the increasing rate of EDTA (mML-1) added to gypsum systems.

EDTA mML^{-1}	ppm					
	P	Fe	Cu	Zn	Mn	Ca
0.0	10.2	0.15	9.2	11.0	12.1	755
0.1	10.0	0.05	7.6	10.8	11.1	745
0.3	10.0	0.08	8.1	10.5	11.1	750
0.5	10.2	0.09	8.3	10.0	10.5	747
0.7	11.0	0.28	10.1	10.6	10.8	770
1.0	12.1	0.87	11.3	11.5	11.8	761
3.0	12.4	6.9	11.1	10.8	10.5	763
5.0	12.8	7.4	10.9	10.8	10.1	771
7.0	14.5	10.1	11.5	11.0	11.2	769
10.0	16.0	11.3	11.8	11.3	11.4	769
15.0	18.1	14.7	15.5	14.6	14.8	779

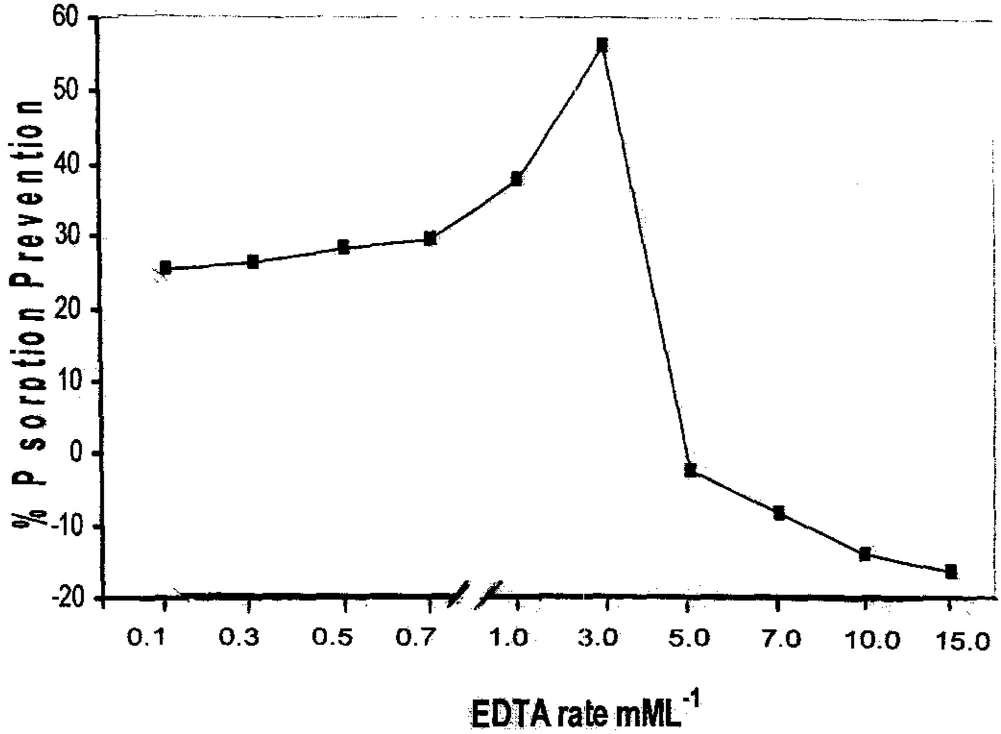

Figure 1: Percentages of the equilibrium P sorption prevention and those of P sorption as functions of increasing rate of EDTA under the Calcite Systems.

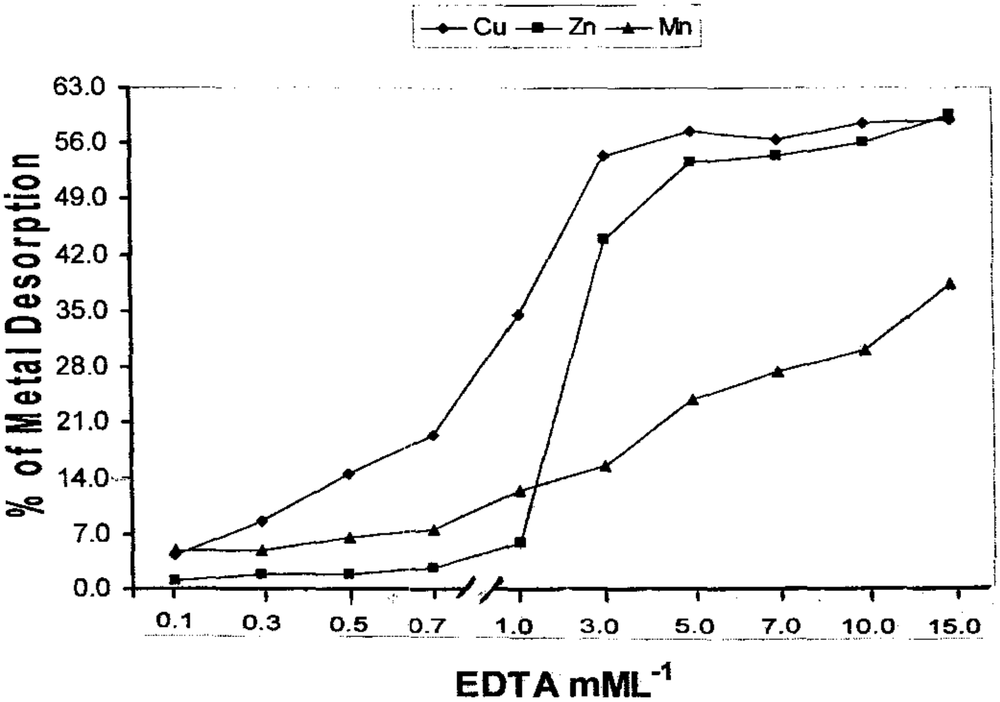

Figure 2: Percentages of the equilibrium desorption of metals as a function of the increasing rate of the EDTA under the Calcite Systems.

DISCUSSION

- EDTA vs. P sorption prevention under Calcite Systems:

From Table 1, one can notice that compared to the control, there was a gradual increase, and then a sudden significant decrease (sorption) in the equilibrium P due to the increasing rate of the EDTA. Nevertheless, Figure 1 shows that approximately 25.0% of the added P was prevented at 0.1 mM EDTA L^{-1} compared to the control. Such increase in the recovered P continued gradually and attained its maximum value, which was 56% at 3.0 mM EDTA L^{-1}. In contrast, after such rate (3.0 mM EDTA L^{-1}) any further increase in the EDTA rate induced gradual significant sorption in the final equilibrium P compared to the control.

Figure 1 shows that there were 5.5, 8.5 14.0 and 16.5% of P sorption due to 5.0, 7.0, 10.0 and 15.0 mM of EDTA L^{-1} added, respectively. However, such finding indicates that sorption phenomenon took place under the concerned rates. Concerning the case of the equilibrium concentration of the bicarbonate, which may be possibly exchanged for by the EDTA ligand, one can notice from Table 1, that there was no significant change in the equilibrium bicarbonate concentration due to the increasing rate of EDTA, especially within the P sorption category which ranged from 389 to 400 ppm of HCO^{-}_{3} . Furthermore, concerning the case of the equilibrium concentration of Ca^{2+}, one can notice that the equilibrium concentration of Ca^{2+} was almost approximately constant, especially within the category range concerned which ranged from 52.2 to 60.1 ppm of Ca^{2+}. According to the pH values within the P sorption category, it is obvious that the sudden significant increase in the equilibrium pH value was found to correspond to the values of p sorption. Such finding might possibly indicate that there was some relationship between the two sudden corresponding phenomena, i.e., the sudden significant rise in the pH values, and those of the corresponding P sorption values. The possible justification for such results may be related to several factors, the most important one being the nature of the chelating ligand. The EDTA with its four negatively charged carboxyl groups had more than one possibility of interaction with the several parameters, that were available in the surrounding reaction media. There were calcite surface sorption sites (exposed calcite crystal Ca^{2+}), soluble Ca^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} as well as K^{+}. The EDTA would repel the phosphate ions, and it would compete with them for the same sorption sites. Whenever the EDTA overcomes the phosphate ions for any sorption sites, especially those of phosphate sorbing or precipitating agents, i.e., the exposed calcite Ca^{2+} or the free Ca^{2+}, the increase in the P solubility would take place and some of the effectiveness of the EDTA toward P sorption prevention, would be attained and this case was confirmed to some extent in the present research, at the first set of the EDTA application rate, which induced 25.0% of the P recovery at 0.1 mM EDTA L^{-1}, and 56.0% of it at 3.0 mM EDTA L^{-1} added (Figure 1). Hence, the question arises about the contradictory trend that suddenly took place at the EDTA application rate of 5.0 mM L^{-1} which showed P sorption phenomenon and induced 5.0% of P sorption and 16.5% of the P sorption, compared to that of the control due to 5.0 and 15.0 mM L^{-1} of the EDTA added, respectively (Figure 1). As it was mentioned above, such contradictory behavior of the EDTA toward P solubility may possibly be related to the corresponding sudden rise in the pH values, under which that opposite trend took place. However, due to the significant sudden rise in the pH value, one would expect a significant increase in the hydroxyl ions, hence the potential of the negatively charged surfaces. The tetra negatively charged EDTA ions, would be compared to the mostly di-negatively charged phosphate ions (under the present system pH), the greater negatively charged EDTA ions would be repelled far away from the negatively charged sorbing surfaces in greater magnitude and by greater repulsion force than those of phosphate ions. Under such possible conditions, the phosphate ions would have a greater chance to be closer than EDTA and sorb on the calcite surface in greater magnitudes and overcome the EDTA in this competition due to this possible mechanism.

Furthermore, Table 1 shows that the equilibrium Ca^{2+} concentration due to the increasing rate of the EDTA did not show any significant positive or negative change. It ranged from a minimum of 42.4 ppm of Ca^{2+} and as a maximum of 60.1 pm of Ca^{2+} due to 0.3 and 15.0 mM of EDTA L^{-1}, respectively. Compared to that of the control which was 50.0 ppm of Ca^{2+}, one would conclude that the EDTA failed to capture or significantly solubilize or bind to Ca cations, as it would be expected under such a case (pH >7). Lindsay and Norvell (1969) reported that the pH of the reaction media would determine which cation (among which Zn^{2+}, Fe^{3+} and Ca^{2+}) is likely to be chelated by the chelating agent of EDTA. They, however, showed that the Zn $EDTA^{2-}$ chelated species predominated in the pH range of 6 to 7, and below this range Fe $EDTA^{-}$ predominated while at higher pH (>7) Ca $EDTA^{2-}$ predominated. However, the results under the present study did not support such a conclusion, but it seemed to be possibly supportive and consistent with what was argued above concerning the issue of the interpretation of the P sorption phenomenon. In addition to the contribution of the resultant P surface sorption which was justified above, one might add that the soluble free Ca^{2+} ions, that were not chelated by the EDTA as well were other sinks for the free phosphate ions, that might react with them and precipitate as insoluble Ca – phosphate compounds. Therefore those two possible mechanisms may justify the present contradictory behavior of the EDTA toward P sorption prevention.

EDTA vs. heavy metals – desorption under absolute calcite systems:

Table 1 shows that the equilibrium concentrations of control values Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} were almost sorbed and only <0.05, 0.04, 0.14 and 1.5 ppm of Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} were respectively detected in the final equilibrium solution. From the same table, one can notice that Fe^{3+}

disappeared totally from all the equilibrium solutions under, all the ten EDTA rates employed, which was less than 0.05 ppm in all. The equilibrium Cu^{2+} concentration was increasing gradually starting from 0.9 ppm (which corresponded to 4.5% of the Cu^{2+} desorbed) as a minimum of desorbed Cu^{2+} and as a maximum of desorbed Cu^{2+} of 11.9 ppm (which corresponded to 59.9% of Cu^{2+} desorbed due to 0.1 and 15.0 mM L^{-1} of EDTA added, respectively.

On the other hand, under the Zn^{2+} case, a general gradual increase trend was noticed (Table 1), but it was not as significant within the rates of 0.1 to 1.0 mM L^{-1} of the EDTA applied which was 0.22 (which corresponded to only 0.4% of Zn^{2+} desorbed) of the equilibrium Zn^{2+}. However, a significant positive change in the equilibrium Zn^{2+} concentration was noticed at 3.0 mM L^{-1} of the EDTA added, and which was 8.8 ppm (which corresponded to 44.0% of Zn^{2+} desorbed of Zn^{2+}). Furthermore, any extra application of the EDTA after the 3.0 mM L^{-1} rate showed no significant increase in the Zn^{2+} desorption which ranged from 10.7 ppm (which corresponded to 53.5% of the Zn^{2+} desorbed) due to 5.0 mM L^{-1} of added EDTA to 11.9 ppm (which corresponded to 59.5% of Zn^{2+} desorbed) due to 15.0 mM L^{-1} of the EDTA applied. Table 1 also shows that the Mn^{2+} was generally the least metal desorbed by EDTA. Although Mn^{2+} was the least sorbed compared to the rest, hence, it was the least desorbed by the application of the EDTA as well. The EDTA desorbed only 5.0% of sorbed Mn^{2+} at 0.1 mM L^{-1} of EDTA added and such level did not change significantly until it reached 12.5% of the Mn^{2+} desorbed due to 10 mM L^{-1} of the EDTA applied. However, a gradual increase which attained its maximum desorption level at the highest rate of the EDTA applied (15.0 mM L^{-1}) and was 9.2 ppm of the equilibrium Mn^{2+} (which corresponded to 46.0% of Mn^{2+} desorbed).

Such findings which showed some differences in the EDTA chelating behavior toward different metals may be attributed to the different chelating affinities that were exerted by the chelating EDTA agent to different metals. Under the present study systems, standard calcite systems, there were several metal cations (Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+}) in addition to Ca^{2+} cation which would be generated by calcite contribution. Thus, a competition phenomenon would take place among these cations for the chelating agent. The strength of the bond formed between the chelating agent and the chelated metal would determine which metal among the rest would have the greatest affinity to the chelating agent. However, such affinity had been reported to be pH dependent. Nevertheless, from their theoretical study of the stability – pH diagrams development, Lindsay et al. (1967) and Norvell (1982) showed that under competition conditions among Zn^{2+}, Fe^{3+}, Ca^{2+} and H^{+}, Fe $EDTA^{-}$ was predominant below pH 6 after which Zn $EDTA^{2-}$ predominated in the pH range of 6 to 7, while at the higher pH values Ca $EDTA^{2-}$ was the predominant form. Although the present standard closed calcite systems should have dealt with systems of controlled pH values of greater than 7.0 and exceeded 8.0^{+} in the final set of the treatments as was indicated and justified above, such conditions have not shown a meaningful support in some parts, the above mentioned conclusion of those investigations mainly with the issue of calcium.

Furthermore, instead of expecting more Ca^{2+} influx to the solution due to expected calcite dissolution by the EDTA agent, our data did not show any noticeable difference in the equilibrium Ca^{2+} concentration compared to the control due to the increasing rate of the EDTA application. However, such result may be possibly attributed to the low rates of the EDTA employed that were not able to induce significant Ca^{2+} dissolution. Moreover, Ca^{2+} was not chelated by EDTA in noticeable values (Table 1) and hence its behavior under our research did not obviously support Lindsay's et al. (1967) conclusion, at least in this context. On the other hand, the rest of our data concerning metals (Table 1) may have supported Lindsay's conclusion in the other parts, especially those related to Fe^{3+}. Table 1 shows that Fe^{3+} was totally sorbed due to all rates of the EDTA. Accordingly, (under pH 7.0^{+}) Fe^{3+} might be precipitated as carbonates or hydroxides, or sorbed on the calcite surfaces. However, taking into account some variabilities, Cu^{2+}, Zn^{2+} and Mn^{2+} were chelated by the EDTA in different magnitudes. The chelating affinity towards these metals followed generally the order of $Cu^{2+} > Zn^{2+} > Mn^{2+}$. Figure 2 shows the percent of the metal desorption due to the different rates of the EDTA application. Note that the percent desorbed of the Cu^{2+} attained its minimum value at the lowest rate (0.1 mM L^{-1} EDTA) which was 4% and increased significantly until it reached 54.5% at 3.0 mM L^{-1} of EDTA application after which the percent of the Cu^{2+} desorption increase was not significant where it reached its maximum level at the highest rate of the EDTA application (15.0 mM L^{-1} EDTA).

On the other hand, the percent of the Zn^{2+} chelation was not significant at the lower rates of the EDTA applications where it attained 1.1% and 6% at 0.1 and 1.0 mM L^{-1} of EDTA applied, respectively, but it suddenly jumped to 44% and then to 53% at 3.0 and 5.0 mM L^{-1} of the EDTA applied. The next rates of the EDTA application induced insignificant Zn^{2+} desorption where it was 54.5, 56.0 and 59.5% of the Zn^{2+} desorption due to 7.0, 10.0 and 15.0 mM L^{-1} of the EDTA application. Moreover, the least chelated metal was Mn^{2+} and the percent desorbed of it attained its minimum at 0.1 mM L^{-1} of the EDTA applied which was 5.0% and then increased insignificantly until it reached 7.5% at 0.7 mM L^{-1} of the EDTA application after which a sudden jump took place at 1.0 mM L^{-1} and then at 5.0 mM L^{-1} of the EDTA added which attained 12.05% and 24.0% of the Mn^{2+} desorption, respectively. The highest percentage of the Mn^{2+} desorption (chelation) was attained at 15.0 mM L^{-1} of the EDTA applied which was 38.5%. Accordingly, such result have obviously clarified that (under the conditions of the present study) the conclusion of Lindsay's and his research team concerning the chelating character of the EDTA especially toward Ca^{2+} , and in some parts toward the rest of heavy metals tested should not be taken as an absolute fact to some extent. Hence, some exceptions may exist as it is documented under the present research project and thus, it must be restricted to its chemical and physical nature of the parameters and all possible variables involved.

EDTA vs. P sorption prevention and heavy metals desorption under absolute standard gypsum systems.

Unlike the calcite systems (namely the control ones) under which the heavy metals were likely to be sorbed due to the presence of the precipitating agents such as carbonate and hydroxyl components, the control treatments (where no EDTA was added) of the gypsum systems should have had not sorbed any of the metals employed since the associated anion to calcium in gypsum compound, the sulfate (SO^{2-}_4), would not form, generally, precipitates with Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+}metals, thus, they should have stayed soluble, to some extent, in the solution. Nevertheless, such a fact was obviously attained, to some extent, under the case of Cu^{2+}, Zn^{2+} and Mn^{2+} where they showed significant existence in the control treatments, but such a fact was not held under the case of Fe^{3+} which approximately totally disappeared from solution or was totally sorbed. The control treatments (Table 2) showed that there were 46.0%, 55.0% and 60.0% Cu^{2+}, Zn^{2+} and Mn^{2+}, respectively, in solution. In contrast, there was only 0.75% of the added Fe^{3+} in solution. However, the only determined values of equilibrium pH and EC were those of the triplicated values of the control treatments (which contained P and metals without any EDTA application). Neither sulfate nor those of the equilibrium pH and EC values were determined under EDTA application treatments. The mean value of the triplicated equilibrium pH of the control was 4.5 and that of the EC was 4.2 mmohs Cm^{-1}. Accordingly, under such acidic conditions, the issue of the equilibrium Fe^{3+} solubility of the control treatment may be possibly, theoretically, partially justified. Under acidic solution conditions provided the presence of $H_2PO^-_4$, Fe^{3+} might form some suggested precipitates that were likely to possibly form under such conditions. Nevertheless, although one of the suggested form needs further detailed studies to be confirmed, in addition to its stability and the pH range under which it exists, it was only hypothesized in order to justify the significant sorption of Fe^{3+} under the present research systems. Moreover, under the control acidic gypsum system, the presence of KH_2PO_4 and Fe Cl_3 may possibly lead to the formation of a possible suggested precipitate like $FeSO_4H_2PO_4$. If this was the case, then the Fe sorption might possibly be justified. Under the acidic soil conditions, one form of the well confirmed Fe phosphate precipitate was $Fe(OH)_2H_2PO_4$, where the silicate minerals could offer the hydroxyl ions which were incorporated in such formula, hence, the gypsum systems under investigation were suggested to provide the sulfate ions instead of the hydroxyl ions and was proposed to precipitate Fe^{3+} in a suggested form ($FeSO_4H_2PO_4$) which corresponded to but not the same as that of the well known one. Table 2, however, shows that Fe^{3+} sorption insignificantly increased due to the addition of the EDTA at 0.1, 0.3 and 0.5 mM L^{-1} of the EDTA rates after which it started to be slightly desorbed at 0.7 and 1.0 mM L^{-1} of EDTA which corresponded to 0.28 (0.65% of Fe desorption) and 0.87 ppm (3.6% of Fe desorption) of Fe^{3+} in solution, respectively. However, a sudden significant increase was observed at 3.0 mM L^{-1} of EDTA which attained 6.9 ppm (33.75% of Fe desorption) of Fe^{3+} in the equilibrium solution and such increase trend was found to be significant at 7.0 and 15.0 mM L^{-1} of the EDTA additions which attained 01.1 ppm of Fe^{3+} (49.75% of Fe^{3+} desorption) and 14.7 ppm of Fe^{3+} (72.75% of Fe^{3+} desorption), respectively. Moreover, such behavior of the EDTA chelating agent toward Fe^{3+} desorption was not significantly detected within the first set of the EDTA application rates namely those of 0.1, 0.3, 0.5, 0.7 and 1.0 mM L^{-1} of the EDTA application. The significantly detected Fe^{3+} desorption levels were noticed in the second set, namely 3.0, 5.0, 7.0, 10.0 and 15.0 of the EDTA application rates which started with a sudden significant jump at 3.0 mM L^{-1} and attained 33.75% of Fe^{3+} desorption and reached its maximum level which was 72.75% of Fe^{3+} desorption at 15.0 mM L^{-1} of the EDTA addition. Some possible interpretation for such behavior may be attributed to the possible variations in the competition strength induced by the EDTA anion against those of $H_2PO^-_4$ and SO^{2-}_4 for Fe^{3+} (and the other metal cations in the system). Under a system of acidic conditions (the systems equilibrium pHs were possibly expected to stay around the pH of the control) the EDTA ion was expected not to fully dissociate, thus some of its reactive groups would remain H - protanated. The EDTA would then be partially negatively charged (this depends on the dissociation constants of the EDTA). It is well known, however, that the highest efficiency of the organic acid to accomplish its role toward the sorption phenomenon would be attained when the pH of the media equals the pK of the acid, i.e., when the acid is half dissociated ($EDTA^{2-}$). Under such conditions, one possible association between the Fe^{3+} and the EDTA would produce FeH_2EDTA^+. Thus, one possible suggested form of Fe^{3+} plus H_2EDTA^{2-} and $H_2PO^-_4$ under such conditions would possibly be $FeH_2EDTA\ H_2PO_4$. If it turns out that this was the case, then such possible combination may contribute to either an increase or decrease in the solubility of either Fe^{3+} or P in the final equilibrium solution depending on the value of the solubility product constant with such suggested component. However, according to the final equilibrium concentration of P and Fe^{3+} (Table 2), one can notice that approximately 50% of the originally applied P was sorbed at no addition (control) of the EDTA and such amount of sorbed P stayed approximately the same until 0.7 mM L^{-1} of EDTA applied, then it started to decrease (compared to the control) at 3.0, 7.0, 10.0 and 15.0 mM L^{-1} of applied EDTA which corresponded to P sorption of 38.0, 27.5, 20.0 and 9.5% of the added P, respectively, thus there was a significant desorption (P sorption prevention) trend in the equilibrium P which was more pronounced within the last set of the EDTA rates where it reached its maximum level (a net of 39.5% of P was prevented compared to the control) at 15.0 mM L^{-1} of the EDTA applied. Furthermore, there was a corresponding desorbing trend noticed in the case of Fe^{3+}. Table 2 shows that the solubility of Fe^{3+} was increasing (desorbing trend) with a sudden jump at 3.0 mM L^{-1} of the EDTA addition and attained its maximum (72.75% of desorbed Fe) desorption at 15.0 mM L^{-1} of the EDTA. It turns out that the suggested $FeH_2EDTA\ H_2PO_4$ formula may possibly hold both Fe^{3+} and P soluble in the equilibrium solution but the EDTA efficiency as a solubilizing agent would be more pronounced in the final set of its application rates, especially in the case of Fe^{3+}.

The metal sorption of the mean levels of the control values (Table 2) were 55.0, 45.0 and 39.5% of added Cu^{2+}, Zn^{2+} and Mn^{2+}, respectively. However, the addition of EDTA induced some insignificant variations in their equilibrium concentrations. Copper was slightly desorbed at 0.1, 0.3 and 0.5 mM L^{-1} of EDTA additions and started to slightly gradually irregularly desorb at 0.7 and 15.0 mM L^{-1} of the added EDTA which corresponded to 4.5 and 31.5% of the Cu^{2+} desorbed compared to the control. On the other hand, EDTA induced only 23.0 and 13.5% of Zn^{2+} and Mn^{2+} desorption, respectively, at the highest rate of it.

ACKNOWLEDGEMENTS

I would like to deeply thank my friend, Professor Abdulaziz M. Al-Bahrani for his assistance concerning computer work and other aspects. I also wish to thank Mr. Mondhir R. Al-Kwaity, an undergraduate student from our department for some lab work in a special study. Special thanks must also be extended to the staff of the Chemical Analysis Laboratory of Saudi Aramco at Al Uthmania Plant, especially to Mr. M. H. Al-Abdullah for the metal analysis by their ICP instrument.

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الملخص العربى

تحرير كاتيونات الحديد و النحاس و الزنك و المنجنيز و حماية الفوسفور من الإدمصاص بفعل ال EDTA فى نظم قياسية تحتوي تلك المعادن بمعية الجير و الجبس

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لقد تم دراسة تأثير حمض ال EDTA على حماية الفوسفور من الإدمصاص وكذلك تحرير المدمص من كاتيونات الحديد و النحاس و الزنك و المنجنيز فى نظم قياسية من الجير و الجبس كل على حده.لقد تمت مفاعلة تركيزات ثابتة (٢٠ جزء في المليون من كل كاتيون) من كل من الحديد و النحاس

و الزنك و المنجنيز على صورة كلوريدات مع وزن ثابت (٢,٥ جم) من كل من الجير أو الجبس كل على حده و لمدة ٢٤ ساعة ثم تلا ذلك إضافة تركيز ثابت من الفوسفور (٢٠ جزء في المليون) بالترافق مع تركيزات متزايدة من ال EDTA إلى محاليل المرحلة السابقة وفوعلت المخاليط لمدة ٤٨ ساعة . و في الراشح فقد أظهرت النتائج بأن ال EDTA تمكن من حماية ما مقداره ٢٥% و ٥٦% من الفوسفور المضاف عند تركيز ٠,١ و ٣,٠ مليمول من الكربون العضوي / لتر من ال EDTA على التوالي ضمن نظام الجير . وفجأة حدث إدمصاص رافقه إرتفاع مفاجئ في قيم ال PH عند التركيز ٥,٠ مليمول ك. ع / لتر EDTA . ومن جهة آخرى فأن النتائج في نظم الجبس كانت مضلله بصفة عامه و هنالك فأن ال EDTA تمكن من حماية مامقداره ٣٩,٥ % من الفوسفور المضاف عند أعلى تركيز منه . وفي نظم الجير فأن ال EDTA لم يتمكن من تحرير كاتيون الحديد عند جميع التركيزات المضافه منه بينما تمكن من تحرير ٥٩,٠ %و ٥٩,٥ %و ٣٨,٥ % من كل من النحاس و الزنك و المنجنيز على التوالي عند التركيز الأعلى منه . و من جانب آخر فأن تحرير كاتيونات المعادن بفعل ال EDTA ضمن نظم الجبس كانت ذات سمه مضللة لجميع كاتيونات المعادن تحت الدراسة. وعلى كل حال و في ضمن نظم الجبس فأن الإدمصاص الشديد الذي لوحظ في كاتيون الحديد في معاملات الشاهد وتحت المعدلات الدنيا من ال EDTA عزيت نظريا إلى تكون مترسب مفترض (Fe SO4H2PO4) يحتمل تكونه تحت ظروف قيم منخفضه من ال PH (PH=4.5) . يضاف إلى ذلك فإن نتائج هذه الدراسة لم تظهر ذوبان ملحوظ في مادة الجير تحت مستوى المعدلات المستخدمة من ال EDTA في هذه الدراسة .