Modeling of ^{36}Cl Transport and Water Flow in Amended Gypsiferous-Calcareous Soil

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Abstract

Dissolution of gypsum has great influence on water flow and solute transport occurring in gypsiferous-calcareous soils. Many models based on convection and diffusion processes have been developed to describe transport in soil. Constraints of estimation of transport parameters in gypsiferous-calcareous soils are mainly due to gypsum influence .The objectives of this study, were to i: modeling the transport of solute (^{36}Cl) in gypsiferous-calcareous soil treated with fuel of FO on dissolution of gypsum associated with calcium carbonate content. Radiotracer of chloride as carrier free of ^{36}Cl was applied to surfaces of saturated soil columns that have 20, 250 and 500 g kg^{-1} gypsum treated with 0, 1, 2, and 4% of fuel oil and leached with water until complete displacement of chloride. During leaching, samples of effluent were collected and measured for Cl^{36} . The application of 1 to 2% FO improved the transport properties due to modification in soil structure. The applied models gave good fit between measured and predicted breakthrough curves of ^{36}Cl with significant linear correlation coefficient (r) that ranged between 0.972 and 0.999. They gave a calculated dispersion coefficient (D) ranging from 2.1 to 79.2 cm^2 day^{-1}, and retardation factor (R) ranging from 0.92 to 1.58. It was found that D was also linearly related to pore water velocity (v). Also, the results indicate the possibility of predicting the distribution of chloride in gypsiferous-calcareous soil for different time periods using correct boundary conditions. Experimental results show that gypsum dissolution in the soil columns is mainly determined by the flow velocity, soil saturation and then partially coating with FO. The role of lime was not well explained in reducing gypsum dissolution because the co-existence of gypsum and lime is not clear enough.

Keywords: Gypsiferous-calcareous soil, ^{36}Cl, solute transport, CDE equation, Breakthrough curves, Fuel oil

نمذجة انتقال الكلوريد-36 وجريان الماء في تربة جبسية_كلسية مصلحة

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الخلاصة

إن لتحلل الجبس تأثير كبير في جريان الماء وانتقال المذاب في الترب الجبسية–الكلسية. استخدمت وطورت العديد من النماذج الرياضية المستندة إلى عمليات الحمل والانتشار لوصف الانتقال في التربة. ولكن محددات تقدير معايير الانتقال في الترب الجبسية ترجع بشكل كبير إلى تأثير الجبس. إن الهدف من هذه الدراسة هو i: نمذجة انتقال المذاب (^{36}Cl) في تربة جبسية معاملة بزيت الوقود بالاستناد على نموذج انتقال الحمل– الانتشار و ii: تحديد تأثير اضافة زيت الوقود في تحلل الجبس وعلاقته بمحتوى كاربونات الكالسيوم (الكلس) في التربة. أضيف الكلوريد المشع إلى سطوح أعمدة تربة مشبعة تحتوي على 2 و 25 و 50 غم كغم$^{-1}$ من الجبس ومعاملة بـ 0، 1، 2، 4 % زيت الوقود. غسلت الأعمدة بالماء لحين الإزاحة الكاملة للكلوريد، وجمعت أثناء الغسل عينات من الراشح وقيس فيها (^{36}Cl). أوضحت النتائج إن إضافة 1.0 الى 2.0 % زيت الوقود حسن خصائص الانتقال نتيجة للتحوير الحاصل في بناء التربة. اعطت النماذج المستخدمة مطابقة جيدة بين منحنيات الاختراق المقاسة والمحسوبة وقد تراوح معامل الارتباط بين 0.972 – 0.999. كما تراوحت قيم معامل التشتت (D) بين 2.1 إلى 79.2 سم^2 يوم$^{-1}$ وعامل الاعاقة (R) بين 0.92– 1.58، وان معامل التشتت يرتبط بعلاقة خطية مع سرعة الماء في المسام. أوضحت النتائج كذلك امكانية التنبؤ بتوزيع الكلوريد في تربة جبسية–كلسية لمدد زمنية مختلفة باستعمال ظروف حدود صحيحة. وتبين كذلك ان انحلال الجبس في اعمدة التربة يتحدد بشكل أساسي من خلال سرعة الجريان وتشبع التربة، ثم بالتغليف الجزئي بزيت الوقود. لم يتبين دور الكلس بشكل واضح في تقليل انحلال الجبس لان العلاقة بين الجبس والكلس غير واضحة بما فيه الكفاية.

INTRODUCTION

Gypsiferous soils are soils that contain gypsum which is hydrated calcium sulphate ($CaSO_4.2H_2O$) in considerable amounts. According to Al-Kaabi (2007) gypsiferous soils cover about 27-36% of the territory of Iraq. When gypsum is present in considerable quantities, the physical and hydrological properties of soil are adversely affected. The dissolution of gypsum is one of the very unfavorable properties of soil. When gypsum dissolves, irregular of land surface sink-holes are formed. Eventually, due to disturbance of soil structure and mixing that occurs due

to the migration of clay particles from the surface horizons of the soil and gypsum crystals to the subsurface horizons of the soil, this causes serious problems in movement of water and solute (Kuechler et al., 2004). Generally, field findings usually indicate that the presence of calcium carbonate and gypsum are conversely found in soil. Number of attempts was made to clarify this phenomenon on the basis of the variation in structure between the two compounds and the presence of dissolved salts in the soil (Al- Barrak and Rowell, 2006, Schonsky et al., 2013). Al-Barrak and Rowell (2006) concluded that the protection of gypsum from dissolution by the formation of calcite coatings has been found to depend on the amount of gypsum initially present and   on   the conditions under which dissolution takes place. The prediction of solute transport is very important in management of gypsiferous-calcareous soil. This could be aided by the application of models particularly those based on convection-dispersion processes. These models consider solute transport mechanisms are due to diffusion plus dispersion and by mass flow or convection with water as the water moves through the soil (Radcliff and Simunek, 2010). Experimental investigations have mainly been focused on data characterizing dissolution of gypsum and their effects on soil characteristics. It is necessary to test how far gypsum transport may facilitate solute transport in gypsiferous soils. Shihab and Mehdi (2018) found that convection-dispersion equation (CDE) can be used to describe dissolution and transport of gypsum through gypsiferous-calcareous soil. It gave a good correlation to predict gypsum breakthrough curves (BTC) and its content in effluent. Shihab and Fattah (2018) found that the retardation coefficient (R) and dispersion coefficient (D) values for NO_3^- increased with increase of gypsum content at constant lime content. Also, they found that NO_3^- transport decreased with increasing of gypsum content. Chloride-36 (^{36}Cl) is one of the radioactive isotopes of chloride (Cl-35) with half-life ($T_{1/2}$=301000 years). It has been well established that behavior of ^{36}Cl in the environment is similar to that stable chloride (Cl-35). Solute chloride was used as a tracer in solute transport and water flow experiments because it is a conservative non-degradable solute (Dizes and Gonze, 2019). Chloride is soluble anion that quickly moved by water through the soil profile. Thus, due to its high mobility in ionic form, chloride therefore is also a key element in the environmental system. Many studies have been done on Cl⁻ transport in field and soil columns experiments under saturated and unsaturated flow conditions (Abu-Zreig and Abu-Ashour, 2004, Badv and Mahooti, 2005, Gonzalez and Shukla, 2011, Zhou et al., 2014, Dou et al., 2020). It is doubtful however, whether CDE is appropriate for describing solute transport in gypsiferous-calcareous soil due to gypsum dissolution and movement. Among soil conditioners that have been used to improve soil characteristics is fuel oil. Fuel oil as a cheap, available, and high carbon content petroleum by-product can be used in small amounts to improve the characteristics of gypsiferous soil (Shihab et al., 2002, Aziz and Ma, 2011). Studies are needed to examine the behavior of chloride in soils with a high content of gypsum and lime in order to effectively predict solute transport by water movement. Also, the modification of soil structure would include solute displacement and transport parameters. Therefore, the objectives of this study were to i: estimate the transport parameters of soil treated with fuel oil using ^{36}CI as a tracer, ii: evaluate the

applicability of convection-dispersion model in describing solute transport to predict chloride breakthrough curves (BTC) in columns of gypsiferous-calcareous soil, and iii) determine the effect of FO on dissolution of gypsum associated with lime content during leaching.

MATERIALS AND METHODS

Theoretical consideration:

The models were based on the analytical solution of convection-dispersion equation:

$$R\partial C/\partial t = D\partial C^2/\partial x^2 - v\partial C/\partial x \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. [1]$$

and R is retardation factor,

$$R = v_w/v_s \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots [2]$$

where C is the volume-averaged solute concentration, t is time, D is dispersion coefficient, X is distance, v is the average pore water velocity, approximated by the ratio q/θ (where q is volumetric fluid flux density, θ is the volumetric water content), and v_w and v_s are the velocity of water and solute, respectively.

Equation 1 can be solved analytically for the initial boundary condition:

$$C(O,t) = C_0 \text{ and } \partial C/\partial X(\infty,t) = 0 \dots\dots\dots\dots\dots\dots\dots \dots\dots\dots. [3]$$

By assuming that solute distribution inside the column are not affected by an outflow boundary or effluent collection system, and considering the column to be part of an effectively semi-infinite system. Also, by assuming that the concentration is continuous at X= L (length of soil column) (0 ≤ X ≤ L), the following equation can be used for solute transport in soil column in one dimension (Skaggs and Leig, 2002)

$$C_e = \frac{1}{2}erfc\left[\frac{RL-v_t}{2(DRt)^{0.5}}\right] + \frac{1}{2}exp\left(\frac{vL}{D}\right)erfc\left[\frac{RL+v_t}{2(DRt)^{0.5}}\right]\dots \dots\dots. [4]$$

where C_e is relative effluent concentration (C/Co) and erfc (x) is the error function complementary defined as:

$$erfc(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty exp(-\varepsilon)\,d\varepsilon \dots\dots\dots\dots\dots\dots \quad \dots\dots\dots \quad ..[5]$$

An expression for the relative effluent concentration in terms of the number of the pore volumes, V, leached through the column and column Peclet number, P,

$$P = vL/D \dots \quad\dots [6]$$

is defined as

$$C_e(V) = \frac{1}{2} erfc\left[\left(\frac{P}{4RV}\right)^{0.5}(R-V)\right] + \frac{1}{2}\exp(P)\,erfc\left[\left(\frac{P}{4RV}\right)^{0.5}(R+V)\right] \dots \dots [7]$$

The boundary conditions of $-D\frac{\partial C}{\partial X} + vC = vC_0,\ \frac{\partial C}{\partial X}(\infty,t) = 0$ and for initial conditions of $C(0,t) = C_0$ equation 1 analyzed to represents volume-averaged or resident concentration, the result is (Radcliff and Simunek, 2010).

$$C_e = \frac{1}{2} erfc\left[\frac{Rx - vt}{2(DRt)^{0.5}}\right] + \left(\frac{v^2 t}{\pi DR}\right)^{0.5} exp\left[-\frac{(Rx-vt)^2}{4DRt}\right]$$
$$- \frac{1}{2}\left[1 + \frac{vx}{D} + \frac{v^2 t}{DR}\right] exp\left(\frac{vx}{D}\right) erfc\left[\frac{(Rx+vt)}{2(DRt)^{0.5}}\right] \dots \dots [8]$$

Soil characteristics and column experiments

Soil with 20, 250 and 500 g kg^{-1} gypsum and 336, 217 and 180 g kg^{-1} carbonate calcium minerals (lime), respectively were prepared by mixing soil sample from the shallow Ap surface horizon with sample from subsurface C1 from Al-Dor District 150 km north Baghdad, Iraq located at 34°27′27″N 43°47′54″E. The soil is a gypsiferous-calcareous soil classified as a Typic Calcigypsids. Some characteristics of the soil are given in Table 1. The experiment was conducted in the laboratories of the Ministry of Science and Technology (Formerly, Iraqi Atomic Energy Commission, IAEC). The pre moist soil with 20, 250, and 500 g kg^{-1} gypsum was mixed with 1, 2 and 4% of fuel oil (petroleum byproduct) at 33 kPa, mixed thoroughly to reach homogeneity and incubated at room temperature for one month. During incubation water was added to maintain water content at 33 kPa. The fuel oil was brought from Al-Dora refinery. It was characterized by specific gravity of 0.95, viscosity of 120 C stock and carbon content of 850 g kg^{-1}. Samples of the untreated (control) and the treated soils were sieved using 2mm sieve and packed uniformly in Perspex tubes 0.5 m long and 0.12 m inner diameter to depth of 0.30 m with bulk density ranged from 1.27 to 1.30 Mg m^{-3}. To perform leaching experiments, the soil columns were saturated from the bottom with saturated gypsum solution to establish a known initial condition with respect to the ionic concentration of solution phase.

Table 1. Some characteristics of gypsiferous-calcareous soil used in the study

Character	Unit	Surface horizon Ap	Subsurface horizon C1
Texture		Clay loam	+
Sand	g kg^{-1}	309.8	+
Silt	=	382.4	+

Clay	=	307.8	+
Gravimetric water content	33 kPa	0.32	0.21
Electrical conductivity (ECe)	dS m^{-1}	2.2	2.7
pH		7.7	7.9
Calcium carbonate (CaCo$_3$)	g kg^{-1}	336.0	173.9
Gypsum (CaSO$_4$.2H$_2$O)	g kg^{-1}	20.0	675.0
Cation exchange capacity (CEC)	Cmole kg^{-1}	28.2	18.5
Ca^{+2}	mmole L^{-1}	16.8	26.0
Mg^{+2}	=	3.0	2.1
Na$^+$	=	2.4	1.7
SO$_4$ $^{-2}$	=	10.3	20.8
Cl$^-$	=	2.0	2.3
Clay minerals	1. palygorskite (dominant) 2. chlorite-illite 3.smectite		

+ Data not available due to high gypsum content which inhibits dispersion of soil particles

Leaching and measuring of Cl-36

Twenty mL of carrier-free Na^{36}Cl solution containing 1.85 MBq (50 µCi) of ^{36}CI was evenly distributed on the surface of each soil column. The columns were then leached by maintaining 0.025 m depth of river water on surface of soil column by Marriott siphon. Samples of the effluent were collected during leaching using fraction collector for measuring activity of ^{36}CI using liquid scintillation counter (LKB 1218 Sweden). Maximum velocity of ^{36}Cl (v$_s$) was calculated from time (t) required for first appearance of ^{36}Cl in effluent samples and the length of soil column (L).   Hydraulic conductivity was also measured as described by Reynolds et al. (2002). Three replicates were used, two close replicates were selected and the third was ignored.

Fitting of models to breakthrough curves

Breakthrough curves (BTCs) were obtained by plotting the relative concentration (C/Co) of solute vs. pore volume (V) and time (t) of leaching. The number of pore volumes is calculated by dividing the amount of water leached through the column (Vt) by the liquid capacity Vo, (Vo= A θ L) of the column:

$$V = V_t/V_0 = V_t/L \dots \dots \dots [9]$$

where A the cross-sectional area of the column. Data were analyzed by MATHCAD software. Estimates for Peclet number (P) and retardation factor (R) were obtained by comparing the experimental curve directly with a series of calculated distributions from Eq.7 and selecting those values of P and R that provide the best fit with one of the theoretical curves (trial and error) and D was calculated from Eq.6. An approximate estimate for R can be obtained first from Eq.2. The relative concentration (C/Co) as a function of time (t) of leaching was also fitted to Eq.4. Soil granules having diameter between 4-9 mm were used to measure mean weight diameter (MWD) (Nimmo and Perkins, 2002). Another two sets of air dry and saturated soil columns that have gypsum content of 250 g kg^{-1} treated with 2% FO were leached in order to verify the accuracy of equation 8 in determining the concentration of chloride remaining in the soil by measuring its concentration in the leachate. Soil from each column was taken out at various

times of the leaching course. Radioactive chloride was measured in a saturation extract. The concentration of chloride measured was compared with that determined from equation 8. Equation 8 was then used to estimate the distribution of chloride in air dried and saturated soil columns at various depths.

RESULTS AND DISCUSSION

Leaching of Cl-36 and breakthrough curves

The measured and predicted ^{36}Cl breakthrough curves (BTC) as function of pore volume (V) for different gypsum and fuel oil content are given in Fig. 1 The shape and position of BTC were differed due to differences in gypsum and fuel oil (FO) content. These differences in BTC reflect the modification occurred in soil structure. Typical BTC (sigmoid shape) are found for the untreated soil of 20 and 500 g kg^{-1} gypsum content. In these curves the passage of one pore volume was sufficient to displace approximately 50% (C/Co=0.5 at 1 pore volume) of ^{36}CI out of columns. The area under the curve up to one pore volume equals that above the curve.
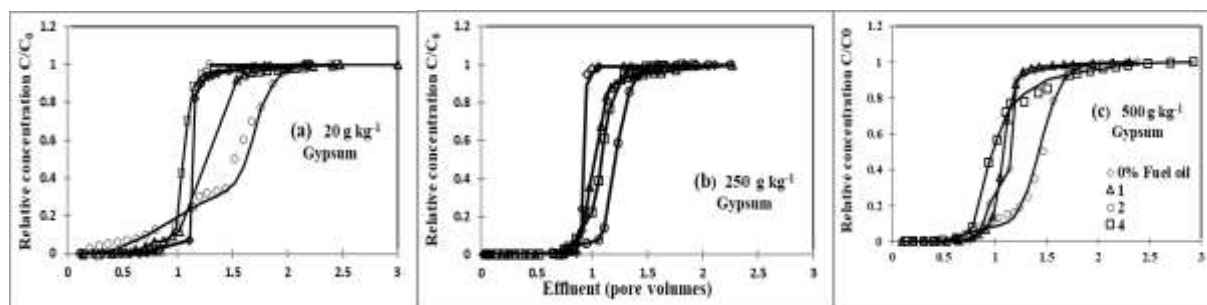

Fig.1. Experimental (dotes) and predicted (solid) line breakthrough curves as function of pore volume for ^{36}Cl displacement at different gypsum and fuel oil contents.

Conversely, for 250 g kg^{-1} gypsum content, about 90% of Cl was displaced after passage of one pore volume. This level of gypsum was reported to be critical level where major (better) changes in physical properties of soil would have occurred. The shape of the BTC explains that Cl tracer is spread as a result of hydrodynamic dispersion (Shukla, 2014, Bourazanis et al., 2017). The dispersion is the dominant mechanism and hence the diffusion can be ignored. The shape of these curves may occur owing to solute mixing that take place by molecular diffusion and variations in water velocity at the microscope level within soil pores. Application of fuel oil greatly changes the shape and position of BTC. The BTC were displaced to the right of one pore volume BTC and showed more tailing and dispersion. These results were observed for the treatments of 1% FO with 20 g kg^{-1} gypsum and 2% FO with 250 and 500 g kg^{-1} gypsum (Fig. 1 and 2). Modification of soil structure due to application of FO caused an increase in aggregate stability. Mean weight diameter (MWD) increased with the increase in concentration of fuel oil for samples that contains 250 or 500 g kg^{-1} gypsum. The average values increased from 1.47 to

2.14 mm compared with 2.54 mm for samples of 20 g kg^{-1} gypsum (Table 2). The chloride transport was greatly affected by aggregate size in results similar to Zhou et al. (2014). The aggregate size had a significant effect on the BTC. The asymmetry of BTC increased with the increase in aggregate size. These differences between curves may be due to changes in either water saturation or pore geometry associated with soil aggregation. The asymmetrical behavior of curves was attributed to increasing disequilibrium for diffusive solute transfer between intra- and inter-aggregate pore water regions. Some of the pore water may be not effective in solute transport due to dead-end pores, the presence of slower or immobile (stagnant) water region, or some other structural feature of geometry (Zhou et al., 2014). The displacement of ^{36}Cl in the stagnant region is by diffusion since water is not flowing. Thus, the advection and mixing of tracer in these pore space negligible. This resulted in a slower movement of tracer, especially at later stage of leaching, and hence the tailing of the BCT. It is seen that time needed to displace C/Co=0.5 of ^{36}Cl is less for 1% FO treatment than for the rest treatments (Fig. 2a). According to Alvarez-Benedi et al. (2005) BTC asymmetric shape also indicates a wide range in the distribution of pore water velocities. They also stated that large holdback area (the area under the curve up to pore
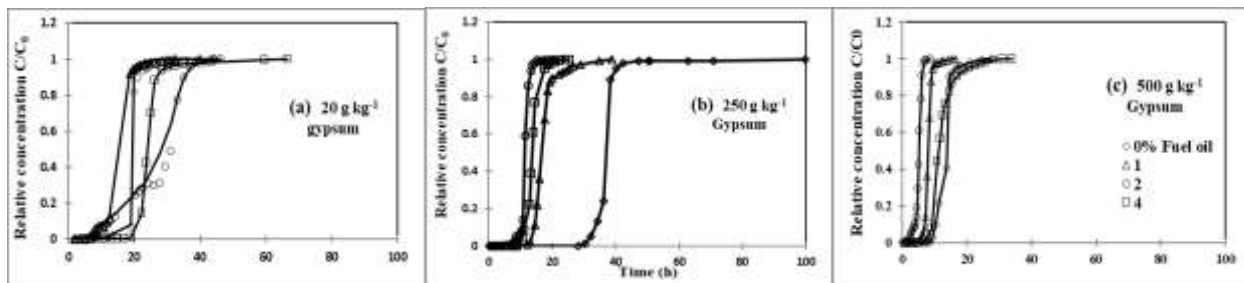

Fig.2. Experimental (dotes) and predicted (solid) line breakthrough curves as function of time for ^{36}Cl displacement at different gypsum and fuel oil contents.

volume 1) indicates difficult displacement, and the tailing or large holdup area (area between BTC and C/Co = 1 from pore volume 1 until end of experiment) indicates large amount of solute that was stored. The chloride BTC shift to right due to pore water velocity increases or holdback decreases. This should happen as more wetted pore spaces are contributed actively in water and solute transport. The results showed that the 2% FO needed less time for 250 and 500 g kg^{-1} gypsum for complete displacement (Fig. 2b and c). Therefore, the time required to displace most of the chloride in untreated soil has increased. These variations in time can be attributed to the fact that the effect of gypsum was greater in the later stages of displacement compared to the first stages due to the low pore water velocity as result of dissolution of part of the fine gypsum crystals. This dissolution led to the mechanical blocking of some pores and impeding the movement of water.

Table 2. Mean weight diameter (MWD) and hydraulic conductivity (K) as influenced by gypsum and fuel oil content.

FO %	MWD (mm)	K (cm d^{-1})
20 g kg^{-1} gypsum		
0	0.09	17.3
1	0.92	24.5
2	3.52	17.3
4	5.62	13.0
Average	2.54	18.0
250 g kg^{-1} gypsum		
0	0.09	8.6
1	0.16	18.7
2	1.03	28.8
4	4.60	23.0
Average	1.47	19.8
500 g kg^{-1} gypsum		
0	0.15	25.9
1	0.12	41.8
2	3.04	82.1
4	5.24	25.9
Average	2.14	43.9

Models fitting to Cl-36 breakthrough curves

The advection-dispersion model gave good fit between measured and predicted BTC data (Fig. 1 and 2) with significant linear correlation coefficient (r). The r values ranged between 0.970 and 0.999 with calculated Chi Square (X^2) value less than tabulated. This indicates a satisfactory applicability of the CDE model to describe the experimental results of gypsiferous-calcareous soil. The model gave dispersion coefficient (D) ranging from 0.5 and 79.2 cm^2 d^{-1}. Higher values were associated with 1% FO mixed with soil having 20 g kg^{-1} gypsum and 2% FO and for soil having 250 and 500 g kg^{-1} gypsum (Table 3). The D of 0.08 cm^2 hr^{-1} (1.92 cm^2 d^{-1}) was for untreated gypsiferous soil having 250 g kg^{-1} gypsum and 0.35-0.60 cm^2 hr^{-1} (8.4-14.4 cm^2 d^{-1}), treated with FO and incubated for 0-6 months. The dispersion coefficient can vary through several orders of magnitude, depending on the mean pore water velocity, its distribution and the size of structural units (Zhou et al., 2014). The tailing increased with increasing D. This may lead to the expectation that the dispersion coefficient increased with the increases in average pore water velocity (v) and MWD. The v was increased with the increased FO and gypsum content. For a given velocity, the asymmetry in BTC increased with increasing aggregate size. Thus, increasing the aggregate size increase the apparent effect of the dispersion provided by the aggregates. Using aggregates with diameter of 0.5 to 4.0 cm and two water velocities, Zhou et al. (2014) showed that increasing aggregate size for a given velocity decreased the diffusion path length, causing incomplete mixing between the chloride solute and pores within aggregates. In addition, they showed increasing pore water velocity decreased the usable residence time for diffusive mass transfer of solutes into and out of the slower flow or immobile region. However,

when the soil columns contained larger aggregates (higher MWD), the presence of a large aggregate and the soil beneath it, which is influenced by its presence, caused an increase in the volume of the immobile region. Consequently, the mobile water fraction decreased with the increase in aggregate size.

Table 3. Transport parameters values estimated by the convection dispersion model at different gypsum and fuel oil content.

Fuel oil %	Dispersion coefficient (D) (cm^2 d^{-1})	Peclet number (P)	Retardation Factor (R)
	20 g kg^{-1} gypsum		
0	13.0	84	1.03
1	31.7	48	1,58
2	30.7	30	1.21
4	7.2	144	1.05
	250 g kg^{-1} gypsum		
0	2.1	660	0.92
1	8.6	135	1.00
2	16.5	135	1.20
4	14.4	132	1.08
	500 g kg^{-1} gypsum		
0	14.4	100	0.96
1	15.8	156	1.08
2	79.2	80	1.40
4	54.7	31	0.98

Fig .3. shows the relation between v and D. the best fit (r^2= 0.6496) is given by the equation:

$D = 0.4043v$……… [10]

The larger dispersivity values causes more dispersion of the solute front will be as a result of a wide range of pore size distribution and pore water velocities (Radcliffe and Simunek, 2010, Shukla, 2014). Shukla et al. (2000) showed that a holdback decreases with increasing pore water velocity. In other words, immobile water decreases with increasing v. He explained this can be due to the higher v which makes possible for chloride to invade stagnant or slowly conducting liquid zones. Jury and Horton (2004) reported that λ values for laboratory experiments with packed soil columns (disturbed) are between 0.5 and 2 cm and for undisturbed soil columns or field experiments are between 5 and 20 cm. Comparing these values with our value of 0.4043 cm for λ can be interpreted by the homogeneity or uniformity of porous media
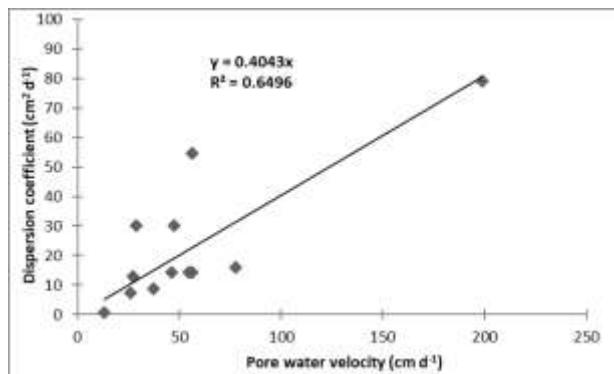
Fig. 3. Dispersion coefficient of [36]Cl as function of pore water velocity for different treatments.

and implies of normal spread of applied solute through the soil column. The equation demonstrates firstly a clear dependence of D on v, and secondly the diffusion is very small and can be neglected. Shihab and Mahdi (2018) showed an increase in D of gypsum with increasing the gypsum content in both continuous and intermittent leaching of undisturbed gypsiferous-calcareous soil columns and explained that the reason for this is due to the increase in the pore water velocity (v), which leads to an increase in the dispersion coefficient due to the decrease in the resident time between the water and the soil. The dissolution of gypsum leads to mixing the soil and the mobility of its components irregularly, which increases the dispersion coefficient D. This means that the dispersion is the dominant mechanism in dissolution and transport of gypsum. The relation between D value and Peclet number (P) (Eq.6) is another important factor for recognizing the effect of P on solute mixing. The Peclet number measures solute movement by mass flow, which is only vertical in the columns, compared with dispersion, which involves advection movement. Although, the effects of both diffusion and dispersion on solute mixing are difficult to be separated, that the P ranged from 30 to 660 (Table 3). This indicates that the dispersion and mixing is the dominate process in transport of [36]Cl. Zhou et al. (2014) explained that the main reason for this was that the CDE model combines the effect of solute transport, and the dispersion coefficient between the mobile and immobile regions, into one term. In general, the small values of D (large P values) observed (Table 3) are indicative of the presence of narrow range in pore water velocities. The retardation factor (R) is another important parameter, which is included in the advection dispersion model and significantly altered the position of the BTC. R values ranged from 0.98 to 1.58 (Table 3). Values of R=1 indicating that no retardation had occurred. The values of R greater than l observed in the soil treated with 2% FO for different gypsum content indicates that retardation had occurred and reflected by the later arrival of tracer in the effluent with tailing. Conversely, values less than 1 indicates only a fraction of liquid phase participating in the transport process or chloride often undergoes anion exclusion from solution close to negatively charged soil particles (Abu-Zreig and Abu-Ashor, 2004), which resulted in a faster leaching of [36]Cl or bypass from a significant portion of the soil solution. When gypsum dissolves, small holes and fissures are formed, and causes preferred-paths transport (Shihab and Mahdi, 2018, Shihab and Fattah, 2018). Differences in R values can be

explained by changing of pore water velocity (v) in which lower R values were obtained at higher v. At higher v, mixing is less and Cl moves faster through the soil. Our results, however, explain that the relationship between v and R less clear, because the range of R is not large. This indicates that chloride behaved as a non-reactive tracer. The preferential flow in the upper part of soil column was increased with the increase in gypsum content and followed by reduction in flowing of water. This reduction was mainly due to mechanical plugging by small gypsum particles which had moved downward. The average hydraulic conductivity (over the three levels of gypsum content) was found to be 17.3, 28.3, 42.7 and 20.6 cm d^{-1} for 0, 1, 2, and 4% FO, respectively (Table 2).

Predicting of chloride concentration

Prediction of change in chloride concentration with depth showed two types of distribution. In the first type (Fig.4a), a rapid and sharp decrease in the concentration of chloride with depth was found during short periods of time not exceeding 10 hours. As for the second type, the decrease in concentration with time was gradual (Fig.4b) and took a longer time that spanned forty hours. This change in concentration was influenced by initially soil moisture, although the two treatments have the same gypsum and fuel oil content. Soil moisture effects chloride transport. When the soil is air dry, the chloride quickly reaches the leachate, and the highest concentration of solute occurs at the wetting front, which leads to the transport of the solute with water in the pores. In this case, the transport is closer to the piston displacement. Upon saturation, the solute delays from the wet front and the water moves by displacing the water already present in the pores. This requires displacement of approximately one pore volume (that is, the volume of water held in the soil column) before the chloride begins to leave the column, and this requires more time. The wetting front in the saturated state moves faster than the air-dry state, but carries with it a small amount of solute. Equation 8 showed good agreement between measured chloride concentration in the leachate and that remaining in soil solution for different time periods (Table 4). The relative error values ranged from 6.4 to 15.8% and 0.7 to 1.3% for air dry and saturated.
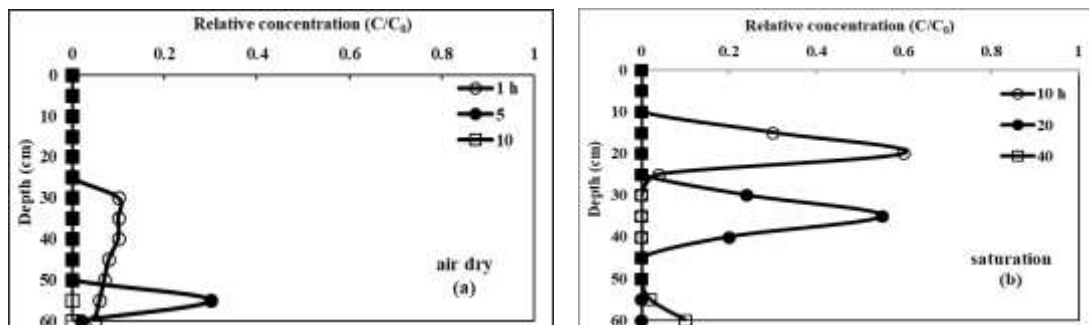

Fig.4. Prediction of chloride concentration in soil at 250 g kg^{-1} gypsum content and 2% FO using eq.8.

soil, respectively. The increase in the relative error of the air dry treatment at 5 and 10 hours is due to the residual chloride remaining in the soil column at these two periods was very small compared to the first period (1 hour) and is represent only a small percentage of the total concentration (C/Co=1), and that any slight difference between the experimental and calculated concentration will lead to amplifying the relative error. This indicates the possibility of predicting the distribution of chloride in gypsiferous-calcareous soil using correct boundary conditions. Application of FO, which is a hydrophobic material, partially coated the soil aggregates, and increased their resistance to breakdown in water. These effects reduced specific surface area, capillary movement of water, and water sorptivity of soil aggregates and thus reduced the solubility of gypsum (Shihab et al., 2002). These researchers found gypsum concentration in the effluent increased during the first stage of leaching, and then it decreased to a specified value which remained nearly constant with further leaching. Also, the obtained results showed that the remaining gypsum content in the soil after leaching course was greater in the columns treated with fuel oil. In addition, the gypsum was accumulated in the middle of the soil columns. Consequently, the above results indicate that dissolution of gypsum is surface phenomenon and the value of dissolution coefficient of gypsum and mass transfer rate depend mainly on the specific area as well as on the sorptivity of soil aggregates. The results show that role of lime was not clear enough in reducing gypsum dissolution. The occurrence of co-precipitation and interwoven between gypsum and lime crystals did not lead to the inhibition of the rate of gypsum solubility as described by Sudmalis and Sheikholeslami (2000) and Schonsky et al. (2013).

Table .4. Relative concentration of chloride (experimental and predicted from Eq.8) remaining after displacement for different periods in soil having 250 g kg^{-1} gypsum treated with 2% FO.

Time (h)	Relative concentration (C/C$_0$)		Relative error (%)
	Experimental	Predicted	
Air dry soil			
1	0.668	0.625	6.4
5	0.082	0.094	14.6
10	0.019	0.016	15.8
Saturated			
10	0.993	1.000	0.7
20	0.987	1.000	1.3
40	0.158	0.160	1.3

$$\text{relative error} = \frac{\text{experimental value} - \text{predicted value}}{\text{experimental value}} \times 100$$

These researchers concluded that the presence of lime strengthened the weak structure of pure gypsum. In comparison with our results, where the content of lime in soils are 336, 217 and 180 g kg^{-1} for the 20, 250, and 500 g kg^{-1} of gypsum content, respectively. It appears that lime may

cause an increase in gypsum hardening in the dry state only due to co-precipitation and interwoven. The precipitation of lime in the soil solution and coating of the gypsum particle surfaces leads to a decrease in the rate of dissolution of gypsum due to the reduction of the available surface area in contact with the solution phase. This depends on the amount of both gypsum and lime present in the soil and on the conditions under which the dissolution occurs, as well as depends on the field conditions at which the coating is formed. Al-Barrak and Rowell (2006) concluded that calcite did not manage to cover the gypsum surfaces when the rate of dissolution of gypsum was rapid, possibly because the surface was continually removed. Slower leaching conditions in the field are likely to help to form coatings and to minimize gypsum dissolution. The experimental results show that gypsum dissolution in the column is mainly determined by the flow velocity, soil water saturation and then partially coating with FO and lime.

CONCLOSIONS

The convection- dispersion model successfully used to predict the concentration of ^{36}Cl in the effluent of gypsiferous-calcareous soil. This model gave good fit between measured and predicted BTC data. Also, FO application modified physical properties of soil. This modification was reflected by the increase in D and R. Higher values of these two parameters were associated with 1% FO mixed with soil having 20 g kg^{-1} gypsum and 2% FO for soils having 250 and 500 g kg^{-1} gypsum. D was linearly related to pore water velocity (v). CDE also showed a good agreement between the measured chloride concentration for the different gypsum content in the leachate and the remaining soil concentration. This means that the distribution of chloride in gypsum soil can be predicted using correct boundary conditions. Application of FO, which is a hydrophobic material, partially coated the soil aggregates, and increased their resistance to breakdown in water. The role of lime was not well explained in reducing gypsum dissolution because the co-existence of gypsum and lime is not clear enough. This needs further research under field conditions to determine the extent to which gypsum dissolution can be reduced. Under these conditions using amendments and slower leaching can be managed and coating may more likely to form.

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