

STUDY OF THE MINERALOGICAL STRUCTURE OF MAIN DOWNSTREAM DRAIN SEDIMENTS AND ITS IMPACT IN BEHAVIOR OF NICKEL AND COBALT

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ABSTRACT

This study was conducted to determine the nature of the mineral structure and properties of carbonate minerals of the sediments of the Main downstream and their effect on the chemical behavior of nickel and cobalt in five areas of Baghdad Governorate: Abu Ghraib, Al-Radwanayah, Al-Yusufiyah, Al-Mahmoudiyah, and Al-Latifayah. The results showed a difference, to the clay minerals of the water stream sediments. The presence of clay minerals such as mica, smectite, true chlorite, and swollen chlorite was observed in varying proportions, and the latter appeared more at the end of the study area. While a decrease in the percentage of kaolinite minerals was observed, a difference was observed in the quantity and properties of carbonate minerals, and the active part of them increased at the end of the study area. The chemical behavior of nickel and cobalt also varied in association with clay and carbonate minerals. The association of nickel with carbonate minerals was greater than that of clay minerals, with a percentage of 53.7, 40.8, 38.9, 40.0, 53.3%, while the association of cobalt with clay minerals was greater than that of carbonate minerals, with a percentage of 49.4, 45.9, 55.4, 45.17, 44.1%, after extracting the association images for each element using the successive extraction technique in all five study areas, respectively.

Keyword: X-ray diffraction; clay minerals; successive extraction; carbonate minerals

المعموري وآخرون

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دراسة التركيب المعدني لترسبات مشروع المصب العام واثرها في سلوك النيكل والكوبلت

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المستخلص

اجريت هذه الدراسة لتحديد طبيعة التركيب المعدني وخصائص معادن الكربونات لترسبات مشروع المصب العام واثرها في السلوك الكيميائي للنيكل والكوبلت في خمس مناطق من محافظة بغداد وهي ابوغريب، الرضوانية، اليوسفية، المحمودية، اللطيفية. اظهرت النتائج وجود اختلاف في طبيعة معادن الاطيان لترسبات المجرى المائي. اذ لوحظ وجود معادن طين كالمايكا والسمكتايت والكلورايت الحقيقي والمنتفخ وبنسب متباينة والآخر ظهر بشكل اكبر في نهاية منطقة الدراسة. في حين لوحظ انخفاض نسبة معادن الكاولنبايت كما لوحظ وجود اختلاف في كمية وخصائص معادن الكربونات وازداد الجزء النشط منها في نهاية منطقة الدراسة. كما تبين السلوك الكيميائي لكل من النيكل والكوبلت في الارتباط مع معادن الطين ومعادن الكربونات. اذ ازيد ارتباط النيكل مع معادن الكربونات بشكل اكبر من معادن الطين وبنسبة 53.7, 40.8, 38.9, 40.0, 53.3% في حين كان ارتباط الكوبلت مع معادن الطين اكبر من معادن الكربونات وبنسبة 49.4, 45.9, 55.4, 45.17, 44.1% بعد استخلاص صور الارتباط لكل عنصر بتقنية الاستخلاص المتعاقب في كل مناطق الدراسة الخمسة على التوالي .

الكلمات المفتاحية: حيود الاشعة السينية، معادن الطين، الاستخلاص المتعاقب، معادن الكربونات



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INTRODUCTION

The Main downstream project is one of the important projects that was completed in the 1990s, and it extends from the regions of central Iraq to its south, with a longitudinal distance of up to 565 km, the total agricultural areas adjacent to this stream reach approximately 1.5 million hectares, cultivated with various crops. It contributes to eliminating the problem of salinization from the farming lands extending along that waterway, It is considered a very large trocar, and the amount of salts and other materials that are thrown into it, represented by waste, is estimated at approximately one million tons annually (10). The chemistry of river sediments related to water stream basins has received great attention from researchers to understand and know the nature of the materials transported by water and the extent to which these sediments are affected by the rate of water flow in addition to the elements carried by water (19, 25). Sediments transported by water are classified based on the method through which these particles are transported and moved. They can either be in the form of plankton or bottom load (38). Suspended sediments may be moved by the turbulent movement of water that faces them upwards. As for the bottom load, they may be transported by rolling, sliding, or bouncing, there is another method of transport, which is the jumping movement, where medium-sized grains move in the water column and then return to the bottom of the water stream. This method depends mainly on the force of water propulsion (20, 36). The elements in the equilibrium medium are exposed to sediments and to many processes that affect the behavior of those elements, such as precipitation, adsorption, complexation, retention, oxidation, and reduction, and this effect is direct through those components in those sediments, which are a homogeneous mixture of organic and mineral materials clay, Many studies conducted before (36, 11 ,40) indicated the role of these components in the adsorption and precipitation of elements. This process varies depending on the element itself, as well as the amount and nature of those components (32), in addition to the effect of the characteristics of the equilibrium medium, such as the

reaction number, electrical conductivity, and the presence of other elements in dissolved or exchanged form in that medium (40, 34). Al-Julmaki (9) indicated that the nature of the variation that occurs in the quantity and quality of minerals carried in water currents can depend on several factors, including the nature and source of those sediments and the rocks derived from them, or the process of mechanical abrasion, physical sorting, dissolution, and chemical weathering, which occur and affect the quantity and quality of minerals in Those sediments. Al-Ali (7) found that the river sediments of the banks and channels of the Shatt al-Arab consist of quartz, calcite, dolomite, and gypsum minerals. As for clay minerals, he found that 37% of them are minerals, montmorillonite, 20% illite, 18% chlorite, and 14% kaolinite. While (5) found a difference in the distribution of clay mineral percentages in the river load related to the surface sediments of the Khor Al-Zubair estuary, A variation was observed in the amount of presence of montmorillonite, kaolinite, chlorite, illite, and palygorskite, This was attributed to the difference in the source of these minerals, the complex hydrodynamic conditions in the region, and the effect of flocculation. He also indicated that the difference in the proportions of these minerals is due to the effect of the carrier agent represented by water. Researcher (29) studied the distribution of heavy elements in the sediment of the Nemunas River in Lithuania, where he found that the concentrations of lead, cadmium, nickel, and manganese exceeded the internationally permissible limits, while they did not exceed the percentage of zinc and copper, this was attributed to the nature of the waste thrown into the river (40). Study was conducted by researchers (31) on sediments of the Ganga River in India, The river sediment was found loaded with high concentrations of heavy elements such as lead, cadmium, nickel, copper, chromium, zinc, This was also attributed to the nature of the materials received by the river. The Main downstream project (Third River) is currently considered a collection of many materials that are thrown into it, in addition to being a trocar, Due to the nature of the climatic conditions that contributed to the lack of water entering this

waterway, which led to its drying in some areas, To know the nature of the sediments present in it in terms of mineral composition and their effect on the accumulation, adsorption and deposition of nickel and cobalt, which are heavy elements. This study aims to identify the effect of mineral composition on the chemical behaviour of cobalt and nickel in terms of adsorption and release.

MATERIALS AND METHODS

In this study, five models of waterway sedimentation for the Main downstream project in Baghdad Governorate were collected from the areas (Abu Ghraib, Al-Ridwaniyah, Al-Yusufiyah, Al-Mahmoudiyah, and Al-Latifiyah). They were given the symbols S1, S2, S3, S4, and S5, which are shown in Figure (1). Chemical and physical analyses of the sedimentation models were conducted according to what was stated in (27, 37). Table (1). shows some chemical and physical properties of sediments. Mineral

analysis of the samples of these deposits was also carried out, relying on X-ray technology, to determine the nature of these mineral components after removing all binding materials and their existing treatment for those deposits at the beginning of S1, the middle of S3, and the end of S5, the study area, The mineralogical properties of carbonate minerals were studied according to what was stated in (24, 40 and 37), The content of these deposits was also estimated from the concentrations of the heavy elements cobalt and nickel and compared with the internationally permissible limits according to the (38). Successive extraction of both elements was carried out to determine the association of each of these elements and its association with the various components of these sediments (clay minerals, carbonate minerals, organic matter, In addition to the mutual and soluble formula), according to the method of (28).

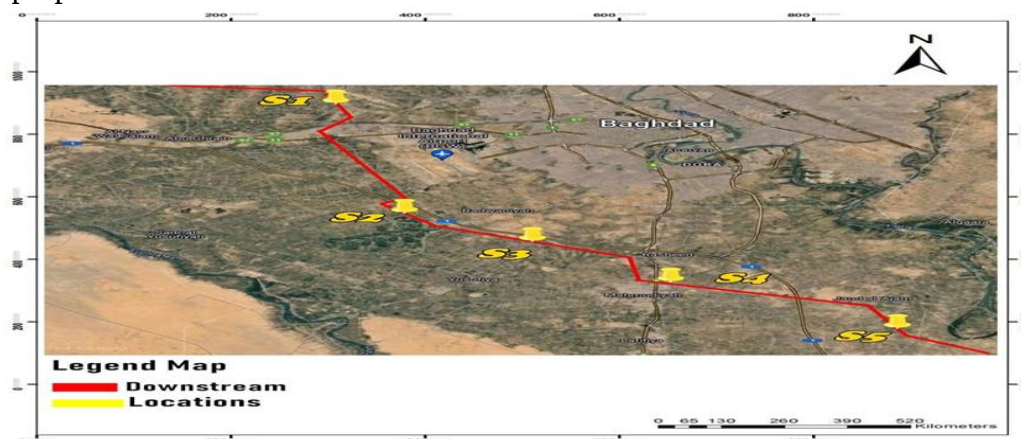


Figure 1. shows the sampling areas

Table 1. Some chemical and physical properties of sediments in the study areas

Properties	Unit	S1	S2	S3	S4	S5
Sand	gm.kg ⁻¹	380	365	305	295	270
Silt	gm.kg ⁻¹	450	346	340	334	315
Clay	gm.kg ⁻¹	170	289	355	371	415
Texture	----	L	C L	C L	C L	C
ECe	dS.m ⁻¹	2.40	3.80	4.72	6.83	7.82
CEC	Cmol ckg ⁻¹	18.3	21.3	23.5	27.7	31.6
O.M	%	1.03	2.28	2.23	2.18	2.02
Gypsum	%	2.5	2.7	3.1	3.5	3.3
Total Carbonate	gm.kg ⁻¹	288.5	269.5	311.2	263.0	277.3
Active lime	gm.kg ⁻¹	97.31	117.23	131.52	155.37	187.51
pH	----	7.9	7.8	8.0	7.9	8.0
Total Co	mg.kg ⁻¹	27.31	39.86	67.81	83.52	70.53
Total Ni	mg.kg ⁻¹	34.9	55.81	62.40	70.73	68.82
Ca ⁺	Meq L ⁻¹	13.01	18.01	23.00	36.45	41.32
Mg ⁺²	Meq L ⁻¹	3.00	5.50	8.01	11.81	10.56
Na ⁺	Meq L ⁻¹	8.90	15.22	16.18	19.73	26.33
K ⁺	Meq L ⁻¹	0.21	0.31	0.40	0.30	0.51
Cl ⁻	Meq L ⁻¹	12.21	16.81	21.16	27.06	33.63
SO ₄ ⁻²	Meq L ⁻¹	10.13	18.11	22.03	33.25	38.53
HCO ₃ ⁻¹	Meq L ⁻¹	1.40	4.41	3.60	7.80	6.88
CO ₃ ⁻²	Meq L ⁻¹	Nil	Nil	Nil	Nil	Nil

RESULTS AND DISCUSSION

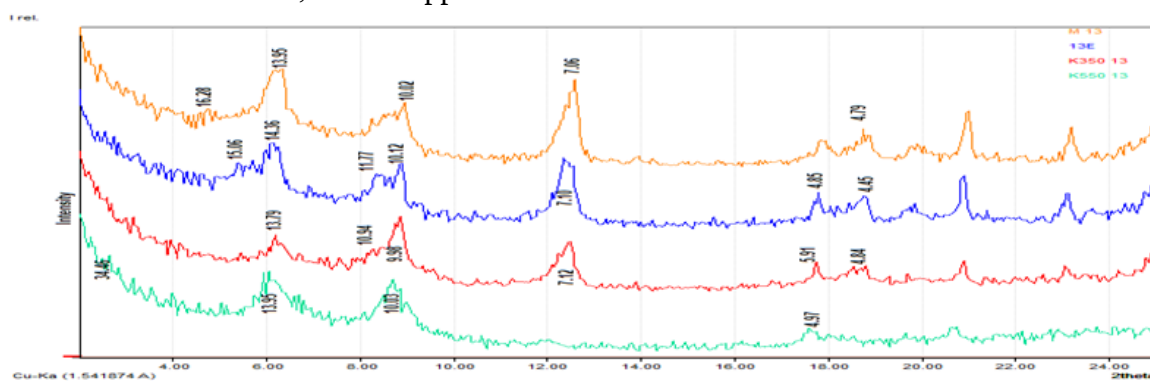
X-ray diffraction analysis of clay minerals:

Mineralogical analysis of clay separations for sedimentation models for the Main downstream project was conducted in the areas of Abu Ghraib S1, Yusufiyah S2, and Latifiyah S3 since water flow in the middle of the watercourse can affect the mineral composition layer, the results of X-ray diffraction analysis at site S1 showed Figure (2). The presence of the regular, layered mineral of the mica-smectite type, was evident at the basal distance of $18.04 \text{ \AA}$, which is close to the basal distance of $19 \text{ \AA}$, which represents the first diffraction of the mix mineral mica-smectite, and this was confirmed by (23). They showed that the limits of the basal distance of the mica mineral are $10 \text{ \AA}$, the basal distance that approaches $9 \text{ \AA}$ is close to the transformed smectite mineral and that the presence of a diffraction of $10.39 \text{ \AA}$ within the treatment when saturated with magnesium and air-drying and its remaining constant in the treatments is confirmation of the presence of the mica mineral in the model. Also, the appearance of diffraction $4.9 \text{ \AA}$, which represents the second diffraction of the mica mineral, with weak intensity in the coefficients, confirms that the mica mineral present is the tri-octahedral mineral. Also, the appearance of diffraction $14.15 \text{ \AA}$ within the treatments saturated with magnesium and air-drying and its transformation to the basal distance of $15.35 \text{ \AA}$ within the saturation treatment with ethylene glycol, to return to that basal distance by shifting at the distance $10.05 \text{ \AA}$ within the saturation treatment with potassium and the treatment at a temperature of 350°C , which confirms the return of the aforementioned metal to smectite, which was originally inherited. From mica mineral. Also, the increase in the diffraction intensity of $10.05 \text{ \AA}$ over the diffraction of $13.50 \text{ \AA}$ in the potassium saturation treatment heated at a temperature of 350°C indicates that the smectite in the model is originally inherited from the mica mineral. The appearance of diffraction $14.46 \text{ \AA}$ in the magnesium saturation and air-dry treatment continues to be present in all treatments, appearing even in the potassium saturation treatment at a temperature of 550°C and at the basal distance

of $13.32 \text{ \AA}$, which confirms the presence of the true heat-resistant mineral chlorite, What confirms this is the presence of diffractions 4.53 and $4.69 \text{ \AA}$, which represents the third diffraction of chlorite within the same parameters. The results also showed the presence of the mineral kaolinite in the model, as the appearance of diffraction $7.28 \text{ \AA}$ in the saturation treatment with magnesium and air drying, continuity and quality in the saturation treatment with ethylene glycol and the saturation treatment with potassium at a temperature of 350°C , and its disappearance in the saturation treatment with potassium at a temperature of 550°C , as this indicates the presence of the mineral kaolinite. As for site S2, X-ray diffraction results showed a large variation in the layer of clay minerals. The results shown in Figure (2) showed the dominance of Montmorillonite, mica, and chlorite of the swollen type, As the appearance of the diffraction $14.03 - 14.55 \text{ \AA}$ in the Mg^{+2} saturation and air-dry treatment and it remains constant in the treatment of saturation with ethylene glycol and saturation with K^+ and heated at a temperature of 550°C , while the third diffraction remains $4.72 \text{ \AA}$ for the chlorite mineral in the last treatment, which confirms the presence of swollen type chlorite within Clay particles, The presence of the aforementioned metal within these deposits may be due to the processes of transport and deposition and the distance traveled by the particles by the carrier agent represented by water, The transport process affects the weathering of this type of mineral and its transformation into open chlorite. Also, the diffraction intensity increases for metals that can expand, such as 1:2 metals, as the basal distance increases with a value of $11.53 \text{ \AA}$, The presence of smectite mineral was clear through the appearance of diffraction $14.16 \text{ \AA}$ in the air-dry saturation treatment with Mg^{+2} and the widening of the basal distance to reach $15.91 \text{ \AA}$ in the ethylene glycol saturation treatment, and it decreases again upon saturation with potassium and at a temperature of 350°C to $10.93 \text{ \AA}$. The appearance of diffraction $10.57 \text{ \AA}$ and diffraction $6.4 \text{ \AA}$ and its continued presence in all treatments confirms the presence of the mineral palygorskite. The presence of this mineral

indicates the layer of the original material containing the gypsum. Also, the presence of diffraction $7.03\text{\AA}^0$ in the air-drying Mg^{+2} saturation treatment, the ethylene glycol treatment, and the ionization with potassium at a temperature of 350°C may indicate the presence of some types of heat-resistant kaolinite that contain large amounts of iron within its crystalline structure. Iron replaces aluminum in the octahedral layer in the kaolinite mineral, and the presence of the basal distance of $17.28\text{\AA}^0$ represents the second diffraction of the uniform, layered mineral chlorite smectite. As for the presence of diffraction $12.31 - 12.87\text{\AA}^0$, it indicates the presence of the irregular, layered mineral mica - smectite. As for the X-ray diffraction analysis in the Latifiyah region S3, which is represented in Figure (3), The results showed the presence of diffraction $14.13\text{\AA}^0$ and the second diffraction at the basal distance of $4.42\text{\AA}^0$, and their remaining constant in all parameters confirms the presence of the true type of chlorite in the model, while the presence of diffraction $10.56\text{\AA}^0$ and the second diffraction $6.37\text{\AA}^0$ while remaining constant in all parameters, confirms the presence of polygorskite mineral in the model. The appearance of diffraction $9.73\text{\AA}^0$ and the second diffraction $4.49\text{\AA}^0$, which appeared in

all transactions, indicates the presence of mica minerals. The presence of diffraction $4.49\text{\AA}^0$ for these minerals, with a low intensity, confirms the fact that the mica present in the deposits of this region is of the tri-octahedral-biotite type. Also, the appearance of diffraction was $14.31\text{\AA}^0$ in the air-dry magnesium saturation treatment, and the widening of the basal distance in the ethylene glycol saturation treatment to reach $15.38\text{\AA}^0$, then its decrease in the K^+ saturation treatment at a temperature of 350°C to reach $10.21\text{\AA}^0$. This was consistent with the increase in diffraction at the expense of the diffraction intensity. $13.69\text{\AA}^0$. This confirms the presence of the mineral smectite and that it is inherited from the mica that has been subjected to weathering. As further evidence of the intensity of weathering due to the influence of the water factor that works to transfer particles from one place to another, is the presence of diffraction $32.71\text{\AA}^0$ during the potassium saturation treatment heated to a temperature of 550°C . This is confirmed by the presence of uniformly distributed minerals of the mica-chlorite type, as well as the presence of diffraction $11.31\text{\AA}^0$ and diffraction. $12.52\text{\AA}^0$ indicates the presence of irregular, layered minerals of the mica-smectite type.



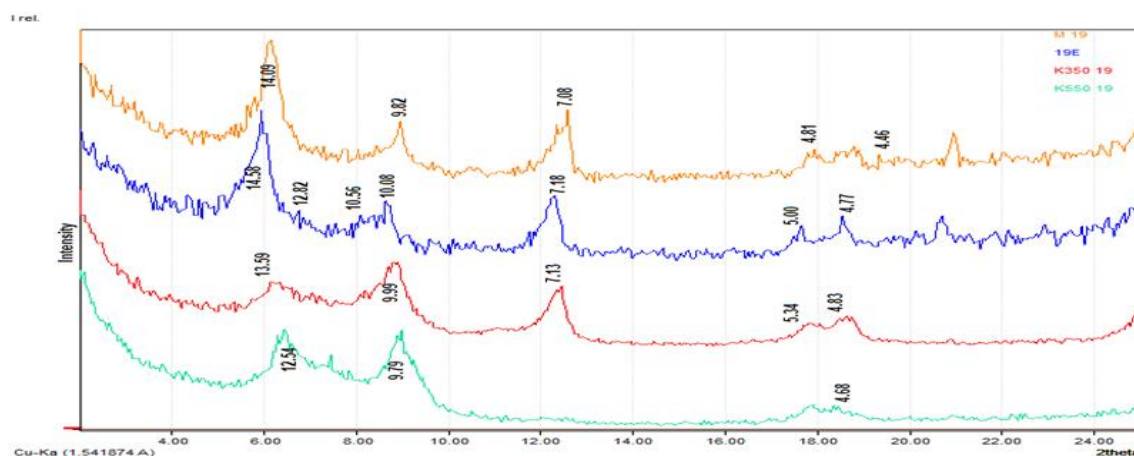


Figure 4. X-ray diffraction analysis of clay minerals in sediments at Site S3

The results also showed the presence of the mineral kaolinite through the appearance of diffraction $7.13\text{\AA}^0$ in the air-dried magnesium saturation treatment, as well as the ethylene glycol treatment and potassium saturation, heated at a temperature of 350°C . The appearance of diffraction $7.32\text{\AA}^0$ when saturated with potassium and at a temperature of 550°C indicates the presence of the true mineral chlorite, which is characterized as a high-temperature resistant mineral. The variation occurring in the clay mineral layer of sediments in the three regions may be due to the effect of the original material and the effect of the water factor, which represents the

transport factor for these deposits, and many factors can affect this, such as the speed of water movement, the length of the distance traveled by the minutes, and the transport capacity. The process of mechanical breakdown and chemical disintegration of the weathering process that occurs in silicate minerals is also important. This is consistent with what was indicated by (21, 15, 16, 17), who showed that the difference in the layer of mineral composition of clay minerals in areas of deposition is due to the effect of the carrier agent represented by water, which affects the chemical weathering of the minerals as well as to the layer of the parent material.

Table 2. Confirmed percentages of the amount of clay minerals in the three sediments areas

The site	Smectite	Chlorite	Mica	Polygorskite	Kaolinite
S1	14.23	30.75	25.37	25.25	4.40
S2	16.17	33.35	26.80	18.51	5.17
S3	19.37	35.12	27.10	12.22	6.19
Rate	16.59	33.07	26.42	18.66	5.25

The results in the table showed a predominance of chlorite and mica minerals compared to other minerals such as smectite, which includes (montmorillonite, badalite, and neutronite), with an increase in the length of the distance within the water stream, which is carried over long distances and deposited due to the decrease in the speed of the water current. This was confirmed by (39), who noticed an increase in the concentration of smectite minerals with increasing distance traveled to the Changlany River and attributed this to the light weight of these minutes and the possibility of transporting them to long distances down the river. The results of the semi-quantitative mineral calculation also showed that the percentage of mica minerals

was high, constituting 26.4%, and its percentage increased with increasing distance in the waterway. This is due to its ease of carrying, being light in weight, and the possibility of re-hanging it after its deposition, which contributes to carrying it over long distances. It was also observed that an increase in the percentage of chlorite minerals increased with the increase in the length of the distance in the waterway, and it constituted a percentage of 33.07% of the total minerals. The increased presence of chlorite minerals, especially the swollen ones (swollen chlorite) within the study area indicates that the internal hydroxide layer of the original chlorite mineral was affected during the water transport process, which is reflected in the filling of the

inner hydroxyl layer, leading to the conversion of chlorite into swollen chlorine. On the one hand, On the other hand, the phenomenon of chlorotization occurs, which occurs in a group of smectite minerals, transforming them into the swollen mineral chlorite, which is one of the phenomena that has been diagnosed in some Iraqi regions, This was confirmed by (16, 13). A decrease in the percentage of palygorskite minerals was also observed with increasing distance in the waterway, the percentage at the beginning of the waterway was 25.25%, while it decreased at the end of the study area until it reached 12.22%. The reason for this may be attributed to the presence of coarse clay particles within it, which settle first due to their high weight compared to the fine clay particles that move with the water over long distances. This was confirmed by (14) in their study. As for the percentage of kaolinite minerals, it recorded a significant decrease in the study areas, as its presence rate in the study area reached 5.49%, and its percentage increased with the increase in the distance traveled by the clay particles with water, Its values were 6.19% at the end of the study area, and the increase in its percentages with the increase in distance traveled is attributed to the fact that this mineral is compatible in its presence with mica minerals, and this was confirmed by (18), who indicated the association of mica and kaolinite in the sites of their deposition.

Characteristics of carbonate minerals in sediments: Table 3 shows the total content and some chemical properties of carbonate minerals, such as the surface area and size distribution of these minerals within the separations, and the nature of their mineral composition in the sediments of the waterway,

The values of these metals ranged between 263.0 - 311.2 g kg⁻¹ soil in S3 and S4, respectively, This variation in the values of carbonate minerals in the study areas is due to several factors, including the layer of the parent material and the special conditions of deposition of these minerals, in addition to the movement of water currents and their impact on the process of transporting or dissolving the particles of these minerals, In general, carbonate minerals are non-clay minerals that are more resistant to weathering, and this depends on the degree of crystallization and the layer of the mineral composition, The values of the total surface area of carbonate minerals ranged from 97.31 to 187.51 m²g⁻¹ for S1 and S3, respectively. The surface area of carbonates is one of the important criteria in determining their effectiveness in the soil, as it gives a true expression of the extent of their contribution in determining the chemical behavior of the elements or influencing other soil properties, such as the degree of interaction and the holding and release of the elements, It can be concluded here that its total content is not expressive This was evident in S3, whose carbonate mineral content reached 311.2 g kg⁻¹ soil, while its total surface area was 131.52 m² g⁻¹ carbonate. The total carbonate mineral content of S4 and S5 was less than that of S3, as it was 263.0 - 277.3 g kg⁻¹ soil, while the surface area of both soils was 155.37 and 187.51 m² g⁻¹, respectively, This is consistent with what was indicated by (30 , 21), in which they emphasized the fact that the total content of carbonate minerals cannot be an accurate criterion in expressing the extent of the effectiveness of these minerals in the soil.

Table 3. Some characteristics of carbonate minerals in the study areas

The site	Total carbonate content g kg ⁻¹	Total surface area m ² g ⁻¹	Size distribution within separations %			Type of carbon metal		
			clay	silt	sand	Calcite	Dolomite	Other carbonate minerals
S1	288.5	97.1	48	36	16	87.33	11.33	1.37
S2	269.5	117.23	44	32	24	88.21	10.0	1.79
S3	311.2	131.52	45	35	20	90.31	8.57	1.12
S4	263.0	155.37	32	38	30	86.40	11.89	1.71
S5	277.3	187.51	21	36	43	88.70	10.38	0.92

Table 3 also shows the variation in the distribution of carbonate minerals within the soil sediments in the study areas, It was

observed that the values of coarse carbonates decreased with increasing distance to the watercourse, in contrast to the soft stone

represented by silt and clay, The values of carbonate minerals associated with the sand were 48, 44, 32, and 21% in S1, S2, S4, and S5, respectively, While the values differed in S3, this difference may be due to factors including the speed of water flow in the source or the effect of the slope factor, As it is known, coarse sediments begin to settle first, and then their quantity increases as the flow rate and steepness increase. As for the sizes of carbonate mineral particles associated with silt and clay, an increase in their values was observed, as they ranged between 32 - 38% and 16 - 43% for sizes equal to the volume of silt and clay, respectively. The fine part increases with the length of the distance that the particles travel with water since light-weight particles can reach greater distances than larger and heavier particles, This is consistent with what was indicated by (15, 2), who indicated that the presence of fine carbonate particles that are the size of clay and silt depends on the intensity of the effect of the weathering factor and the nature of the effect of the agent transporting those particles. The results in the table above also show that there is variation in the layer of carbonate minerals in the sediments of the study area, and this is considered normal due to the variation in conditions of deposition and dissolution, as well as the effect of the parent material, which is considered a sedimentary parent material, The results showed that the percentage of calcite minerals exceeded 87% in all study areas and reached about 90% in study area S3, while the values of dolomite minerals ranged between 8.57 - 11.89%, with its percentage generally lower compared to calcite mineral, This is because dolomite mineral is formed in nature under special environmental conditions represented by high pH values of the equilibrium medium. Magnesium also needs high temperatures to be able to get rid of the water atmosphere surrounding it and enter into the crystalline structure of the metal, and this confirms the fact that what exists of this metal is primary and cannot be formed under the current conditions of deposition of a secondary metal, This is consistent with what (32) confirmed about the effect of carbonate mineral precipitation in different salt environments. It is also noted in the table that

the percentages of other carbonate minerals are very small and do not exceed 2% in all deposits of the studied areas, which means that they are minerals with high solubility compared to calcite and dolomite. Arkonite mineralization, which is similar to the mineral calcite but is more soluble than it, or the magnesium-bearing mineral calcite, which is the mineral resulting from the combination of magnesium as an ion with calcite, which has been observed in various studies in Iraqi environments (11, 34).

Successive extraction of nickel and cobalt in sediments of the study area: Tables 4 and 5 show the successive extraction values of nickel and cobalt and determine their association with the various soil components of clay minerals and carbonate minerals, Both tables also show the values of their melted and mutual forms, The results showed that the nickel element was associated with carbonate minerals to a greater extent than with the mineral components of the soil, represented by clay minerals and even organic ones, at a rate of 53.7, 40.8, 38.9, 40.0, and 53.3%, As for clay minerals, they were 15.9, 24.13, 24.2, 26.28, and 21.8% for S1, S2, S3, S4, and S5, respectively. This may be attributed to the higher affinity of nickel for bonding with carbonate minerals compared to clay minerals. It was also noted that the bonding state of nickel with carbonate minerals also differed, as it was observed that the amount of nickel bound to carbonates increased with the increase in the percentage of active lime, which is shown in Table (1). This is attributed to the increase in the values of the surface area values of carbonate with the increase in the percentage of active lime, and this confirms the fact of the correlation that occurred and increased with the increase in the surface area and the decrease in the particle sizes of the carbonate minerals. The bonding process depends on the nature and type of surface, and this was confirmed by (4, 3, 6, 5, 10). It was also noted that the percentage of dissolved and exchanged nickel bound to the organic matter was very low compared to the total, as it reached 3.7, 3.0, 2.9, 2.7, and 3.9% for the dissolved form, and 16.4, 20.6, 21.6, 22.2, and 13.6% for the exchanged form. With organic matter, the percentage was 10.0, 11.2, 12.0, 8.6, and 7.4% for S1, S2, S3, S4, and S5,

respectively. The decrease in the percentage of dissolved and exchangeable forms associated with the organic matter of nickel in the sediments of the study area has led to the influence of several factors, including those related to the nature of the coupling medium, such as the basic reaction number (pH). Most studies indicate a decrease in the forms of some elements due to their exposure to precipitation and adsorption on the surfaces of

some materials at high levels. The degree of interaction is more than 7. The percentage of organic matter is also low compared to other components, such as clay minerals and carbonate minerals. Also, the existing organic matter did not reach the high efficiency of the effect because it was not decomposed due to the conditions of continuous immersion that prevent its decomposition, and this is consistent with what was reached by (8, 5).

Table 4. Successive extraction of nickel concentrations with soil components. mg kg⁻¹

The site	Total nickel content	dissolved	exchangeable	associated with Carbonet	associated with Organic matter	associated with Clay minerals
S1	34.96	1.32	5.74	18.78	3.51	5.56
S2	55.81	1.73	11.52	22.81	6.28	13.47
S3	62.40	1.87	13.51	24.31	7.53	15.13
S4	70.73	1.93	15.73	28.35	6.13	18.59
S5	68.82	2.75	8.37	36.52	5.13	15.05

Table 5. Successive extraction of cobalt concentrations with soil components. mg kg⁻¹

The site	Total cobalt content	dissolved	exchangeable	associated with Carbonet	associated with Organic matter	associated with Clay minerals
S1	27.31	0.93	2.71	6.89	2.87	13.51
S2	39.86	1.21	6.52	10.45	3.37	18.31
S3	67.81	1.87	7.31	17.35	3.69	37.59
S4	83.52	1.93	8.92	30.15	3.79	38.73
S5	70.53	1.86	8.12	26.15	8.89	31.15

As for the element cobalt, it was noted that its association with soil components differed significantly compared to the element nickel. The amount associated with clay minerals increased compared to the amount associated with carbonate minerals. The correlation rates were 49.4, 45.9, 55.4, 45.17, and 44.1% with clay minerals, while with carbonates, the correlation rates were 25.2, 26.2, 25.5, 36.0, and 37.0%. As for the amount of dissolved and exchangeable elements bound to the organic matter, its percentage was also low compared to the bond with clay minerals and carbonate minerals, the percentage of solute was 3.4, 3.3, 27.5, 2.3, and 2.6%, while the percentage of mutual was 9.9, 16.35, 27.5, 10.6, and 11.5%. As for the association with organic matter, the percentage was 10.1, 8.4, 5.4, 4.5, and 4.0% for study areas S1 and S2, S3, S4, and S5 respectively. The results also showed that the association of cobalt with clay minerals depended on their quantity in each area of the study area, which increased with increasing the length of the waterway and the distance traveled by the clay particles. In general, it was

noted that the concentrations of both elements, which are considered pollutants, increased and exceeded the internationally permissible limits according to the World Health Organization (WHO) system. The increase in the concentrations of these two elements from those sediments to the layer of materials that are thrown into that waterway, which is the waste of factories and laboratories located within the study area, is consistent with the findings of (7, 12, 17, 22, 26). Therefore, it must be pointed out that the chemical behavior of any element in the equilibrium medium depends on the nature of the components of that medium, which is represented in the soil by organic and mineral colloids (clay and non-clay) and the amount of negative charge that that medium carries on the surface, which plays a major role in the process of holding or binding these elements. Which is one of the polluting elements, this condition is a correct condition through which the movement of these elements can be restricted or reduced, and thus their impact on the environment is reduced. This was confirmed by (15, 35, 33).

CONCLUSIONS

It can be concluded from the above study that the chemical behavior of any element in the equilibrium medium, including nickel and cobalt, depends on the nature of the components of that medium, represented by the soil, with its mineral and organic colloids and the amount of negative charge that this medium carries on its surface, it plays a major role in the process of adsorption or release of these elements, which are considered pollutants. This is a correct situation through which the movement of these elements can be restricted or reduced, thus reducing their impact on the environment.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

DECLARATION OF FUND

The authors declare that they have not received a fund.

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