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## Potassium Buffering Potential in Some Burned Soils of North Iraq

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### ABSTRACT

This research was conducted to study potassium buffering potential behavior in some burned soils of Baweza – Mosul and Zawita-Dohuk , in north of Iraq. Potassium forms and the buffering potential phenomenon were studied by using thermodynamic parameters according to quantity- intensity ratio (Q/I) at 298 °K. The main results could be summarized as follows A great affection for the firing process to cause a high potassium availability and lost by leaching. The ARKe value ranged widely from 0.02 to 0.08 (mol L<sup>-1</sup>)<sup>1/2</sup>, the potassium labile pool (LK) ranged from 7.951 to 27.919 cmolc kg<sup>-1</sup>, the potential buffering capacity (PBCK) ranged between 285.47 and 369.48 cmolc kg<sup>-1</sup> (mol L<sup>-1</sup>)<sup>-1/2</sup>, the free energy of exchange (-G) were range between 3291.8 and 4819.8 kJ mole<sup>-1</sup> and the Gapon selectivity coefficient (kG) values fluctuated within the range 8.44 to 12.88 (L mol<sup>-1</sup>)<sup>1/2</sup>. PF values were 0.018 to 0.025 .

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## INTRODUCTION

Although banned in many jurisdictions, the prescribed firing of crop residues is a common activity for some farmers during the annual preparation of land for cultivation and to eliminate weeds and soil pathogens (Stephens et al. 2014). The firing of residues may increase the temperature of the soil surface up to 500°C (Thomaz, et al, 2014). The elevated temperature affects the physicochemical, biological, and mineralogical properties of the surface soils (Akhzariet, et al, 2022). The heating of soils due to the firing of plant residues may affect K dynamics and change soil K forms, release, and fixation. Generally, temperatures higher than 250°C may burn soil organic matter (Ulery, et al. 2017) and release exchangeable K. However, high temperatures may change the structure of K-bearing minerals (feldspars and micas) (Ulery, et al. 1996). Sarikaya, et al. (2000) hypothesize that heating of calcareous soils increases soluble and exchangeable K and consequently K release rate. On the other hand, the K fixation capacity of soils may be limited due

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to the change in the structure of K-fixing minerals and the low diffusion of K ions into interlayer spaces (Wakeel, 2022).

An increase in different forms of K after heating of soils to 350°C may be associated with partial destruction of K-bearing minerals like micas and feldspars and subsequently release of structural K ions to the soil solution. Due to the equilibration among different forms of K, Ks ions may be diffused to exchange sites, and clay interlayer space and K fixation may have occurred (increase in K<sub>ex</sub> and K<sub>nex</sub>). However, as shown, heating of soils to 100 and 225°C had no significant effect on K dynamics (except for K<sub>s</sub>) (Najafi-ghiri and Boostan, 2020). And concluded heating of soils to high temperature may collapse some clay minerals like smectites and decrease diffusion of K into interlayer space and fixation. However, this process may partially collapse smectites, but complete dehydration of expansive minerals may occur at temperatures greater than 500°C. While Morodome and Kawamura (2011) referred that heating to high temperatures may cause dehydration of some cations like Ca, Mg, and Na. These cations may enter the interlayer space and limits K fixation by minerals. Smectites may also fix K ions released after combustion of organic matter and their K fixation capacity may be limited due to conversion to illite. Also Meira-Castro et al. (2014). indicated that some parts of smectite may be converted to illite after several hours of heating in the presence of K ions. This conversion decreases the K fixation capacity of the soil.

The status of K on Iraqi soil has been studied by many investigators (Al-Kanani, et al. 1991; Al-Zubaidi, 2003; Ahmed and Sheikh-Abdullah, 2020). Using thermodynamic methods showed that the rate of release of K from Iraqi soils is very low and this may explain the response of most Iraqi soils to K-fertilizers application in spite of their high content of K, availability of K to plant depends on its intensity, capacity, and renewal rate in soils.

Intensity is the K concentration in soil solution, capacity is the total amount of K in soil solids available to go into the solution (Al-Obaidi, et al. 2019), and the renewal rate is a kinetic factor describing the K transfer rate from capacity to intensity. Potassium exchange-equilibrium parameters were the outcome from the quantity-intensity (Q/I) isotherms, i.e. K equilibrium activity ratio equilibrium, potential buffering capacity for K (PBC<sup>K</sup>). The quantity-intensity (Q/I) concept has been narrowly promulgated in the scientific literature to investigate the K of burned soils. In this approach immediate availability of K is related to the intensity factor, the reserve of non-exchangeable K to the quantity factor, and replenishment capacity to the buffering capacity (Wang, et al. 2004; Bangroo, et al. 2021).

Various attempts have been made to characterize the relationship between intensity and capacity of soil K or soil K buffering characteristics (Evangelou et al., 1994). It was reported that higher values of labile K indicated a greater K release into soil solution resulting from a larger pool of soil K. A higher potential buffering capacity for potassium (PBC<sup>K</sup>) value is indicative of a good K availability while a low PBC<sup>K</sup> soil would suggest a need for fertilization. Some agricultural practices such as K fertilization and liming were found to induce changes in the magnitude of the K activity ratio at equilibrium (AR<sup>K</sup><sub>0</sub>), labile K<sub>Lab</sub> and PBC<sup>K</sup> values (Sparks and Liebhardt, 1981; Wang et al., 2004). If, however, a Q/I is to be of any value in indicating the amount of soil K available for uptake during the growing season, its form must be unaffected by the amount of K fixation or release that is likely to occur during one growing season.

Fergus et al. (2005) Hamed and Amin, (2017) have reported that K uptake by growing plants generally affects the pool of readily available K forms, and moreover, these changes, if considerable, might be expected to alter the form of the Q/I of a soil. Since plant growth is not directly limited by the amounts of exchangeable soil K, therefore it should be necessary to elucidate this phenomenon on the basis of equilibrium studies in order to test the immediate power of soils to supply K to plants. This approach needs the use of the equilibrium (Q/I) concept which should be a good tool, whose application may provide sufficient data about K dynamics soils under plant cropping. Such comprehensive studies are intended to outline some specific information that should clearly determine the capacity of soils for K supply and replenishment (Bernard et al. 2006; Al-Hamandi et al. 2019). The description of the K-parameter provides a wide basis for comparing soils and studying the effect of fire on potassium status.

This study regarded the first research in Iraq aim to evaluate the effect of fire on potassium status in Burned soil in northern Iraq and their fertility evaluation, by using thermodynamic approaches to determine thermodynamic parameters and evaluation of potassium supplying power.

## MATERIALS AND METHODS

This research was conducted to study potassium buffering potential behavior in some burned soils of (Baweza – Mosul Aridisols (36°25'59.52"N 43°08'21.55"E) Cereal Crops and Zawita- Dohuk - Mollisols (36°54'46.3"N 43°08'14.2"E) Forests soil in north of Iraq (Table 1) governorates Studied soils were classified under the main following *orders* as Aridisols, and Mollisols according to USDA (United State Department of agriculture) Soil Taxonomy (Soil Survey, 2017) as shown in (Table 1) . The soil samples were air dried and ground to pass through a 2-mm sieve prior to analysis .The physical chemical and analyses were done as described by (Sparks, 2017; Salim and Ali, 2017). The soluble K was determined from the soil saturation extract .Exchangeable potassium was extracted from the soil with 1M (NH<sub>4</sub>Cl), as the extraction solution, and 1M CaCl<sub>2</sub> solution.Non-exchangeable K was extracted from the soil by using 1M boiling HNO<sub>3</sub> ,the non-exchangeable K was calculated from the difference between the amount of K which was extracted by boiling HNO<sub>3</sub> and the amount which was extracted by 1M CaCl<sub>2</sub>.

**Table (1): Geographical data and morphological description of the locations of the study soil samples**

| Site and rating     | Geographical location (GPS) | Agricultural exploitation |
|---------------------|-----------------------------|---------------------------|
| 1- Mosul (Aridsol)  | 36°25'59.52"N 43°08'21.55"E | Cereal Crops              |
| 2- Dhok (Mollisols) | 36°54'46.3"N 43°08'14.2"E   | Forests                   |

### Potassium adsorption (quantity-intensity) (Q/I) study

It was performed according to the procedure described by Wang et al. (2004) and applied by Bangroo,et,al (2021) (2.00 gm) duplicate samples of the soils were equilibrated in 100 ml polypropylene tubes containing 40 ml of solution containing from( 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, and 2.0 mmol K<sup>+</sup>L<sup>-1</sup> as KCl in 0.01M CaCl<sub>2</sub>. suspensions were shaken for one hour at 298K<sup>o</sup> (Isotherm reaction) and let to equilibrate for 48 hours and then centrifuged. The supernatant were analyzed for K, Ca, Mg, and EC, and the K were determine by flame photometer while Ca, Mg were determined by titration with EDTA disodium salt solution. The EC were measured in each solution by EC-meter.

The change in amount of K in solution gained or lost by the soil (±ΔK) was calculated from the difference in K<sup>+</sup> concentration between the initial and final solutions after equilibration with soil. This amount expressed in (cmol<sub>c</sub>kg<sup>-1</sup>).was calculated according the following equation

$$(\pm\Delta K) = (C_i - C_f) \times V/m \dots \dots \dots (1)$$

Where:

V=Volume of solution cm<sup>3</sup> , m=mass of dry soil Kg

C<sub>i</sub> and C<sub>f</sub> = concentration of potassium before and after equilibrium mg.L<sup>-1</sup>The K intensity factor in liquid phase of soil expressed as activity ratio AR<sup>K</sup>, it was computed from the measured concentration of Ca, Mg and K in the supernatant solution after equilibration. The activity ratio of potassium (AR<sup>K</sup>) was calculated according to Ratio law (Beckett, 1964) as:

$$AR^K = \frac{a_K}{\sqrt{a_{Ca} + a_{Mg}}} \dots \dots \dots (2)$$

$a_i$  = ionic activity species (Ca, Mg and K). The ionic activity was calculated according to the Lewis equation as described by Sposito (2018).

$$a_i = C_i + \gamma_i \dots \dots \dots (3)$$

Where:  $a_i$  = ionic activity.  $C_i$  = the species concentration of ions in mol L<sup>-1</sup>.

The ionic activity coefficients were calculated by the empirical Davies equation given by Sposito (2018) as:

$$- \log \log \gamma_i = 0.512 Z_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \dots \dots \dots (4)$$

$$\log \gamma_i = - 0.509 Z_i^2 [\sqrt{I} / 1 + \sqrt{I} - 0.3 I] \dots \dots \dots (5)$$

Where:  $\gamma_i$  = the mean activity coefficient of the electrolyte.  $Z_i$  = the species valence of ion.  $I$  = ionic strength in mol L<sup>-1</sup>.

$$I = 0.013 * EC \dots \dots \dots (6) \text{ Where:}$$

$I$  = Ionic strength in mol.L<sup>-1</sup> and  $EC$  = dSm<sup>-1</sup>

From a plot of ( $\pm \Delta K$ ) versus the activity ratio the Q/I parameters were obtained. The intercept of the Q/I curve on the  $AR_{equ}^K$  axis, where  $K=0$ , gave the soil K activity ratio at equilibrium ( $AR_{0}^K$ ), which denotes the soil solution K activity relative to the  $Ca^{+2} Mg^{+2}$  at equilibrium. The equilibrium potential buffering capacity for potassium ( $PBC_{0}^K$ ) was calculated as the slop of the linear section of the Q/I curve. The labile potassium ( $\Delta K_0$ ) was obtained from the intercept of the extrapolated linear part of the Q/I isotherm on the quantity axis. The free energy of the K replenishment ( $-\Delta G_{equ}^K$ ) was computed from the following equation

$$-\Delta G_{equ}^K = 2.303RT \log AR_{0}^K \dots \dots \dots (7)$$

Where  $R$  and  $T$  are gas constant and absolute temperature, respectively.

the Gapon selectivity coefficient ( $k_G$ ) should provide good comprehensive and indicative information of K replenishment capacity of the soils. The  $k_G$  calculated as follows:

$$k_G = PBC_K / CEC \dots \dots \dots (8)$$

Where:  $k_G$  = Gapon constant,  $PBC_K$  = Potassium Potential buffering capacity

$CEC$  = Cation exchange Capacity

$$\text{preferential factor (PF} = \frac{K_{ex}}{(Ca + Mg)_{ex}}) C^K / CEC \dots \dots \dots (9)$$

## RESLUT AND DISCUATION

The results values as shown in Table (2) indicated that the fire had a great affection on soil properties, they became a more alkaline reaction. , non-saline calcareous soil (FAO, 2016.) the total  $CaCO_3$  equivalent increased from 160.36 to 261.82 and from 28.63 to 141.45 gm kg<sup>-1</sup> for Baweza and Zawita respectively because burned soil led to more accumulation plants ash that rich in cations like  $Ca^{+2}$  especially that reacted with carbonate ion to precipitate as  $CaCO_3$  (Akhzari et al. 2022). These results indicate that all soil samples are calcareous (FAO, 2016; Zhu et al. 2021). The results also showed that there are different content of organic matter between locations (Zhang, et al. 2020; Zhao, et al. 2022). The amount of soluble ions and exchangeable ions were shown in table (2).

**Table (2): Physical and chemical characteristics of before and after burning in the soils**

| No. | Soils<br>Locations      | before burning |      |      |         |     |                                   |                    | after burning |                       |          |        |        |         |                    |
|-----|-------------------------|----------------|------|------|---------|-----|-----------------------------------|--------------------|---------------|-----------------------|----------|--------|--------|---------|--------------------|
|     |                         | PSD g/kg       |      |      |         | pH  | EC<br>dS m <sup>-1</sup> at 25 °C | CEC<br>cmol<br>/kg | O.<br>M.      | CaC<br>O <sub>3</sub> | PSD g/kg |        |        |         | CEC<br>cmol<br>/kg |
|     |                         | Sand           | Silt | Clay | Texture |     |                                   |                    |               |                       | Sand     | Silt   | Clay   | Texture |                    |
|     |                         |                |      |      |         |     |                                   |                    |               |                       |          |        |        |         |                    |
| 1   | Baweza – Musu Aridi sol | 142            | 526  | 332  | SCL     | 7.8 | 2.29                              | 27                 | 47            | 271                   | 100ns    | 390*   | 510*   | C       | 36*                |
| 2   |                         | 162            | 517  | 321  | SCL     | 7.6 | 2.21                              | 25                 | 42.5          | 259                   | 102.5*   | 457.5* | 440*   | SL      | 33*                |
| 3   | Zawita – Duho           | 238            | 471  | 291  | CL      | 7.5 | 1.69                              | 24                 | 28            | 337                   | 180*     | 350*   | 470*   | C       | 32*                |
| 4   | Molli sols              | 233            | 454  | 313  | CL      | 7.7 | 1.91                              | 21                 | 23.19         | 316                   | 168.6*   | 389.6* | 441.8* | C       | 29*                |

,\*means that significant difference between before and after burning for (Texture & CEC)  
Ns, means that non-significant difference between before and after burning for (Sand)

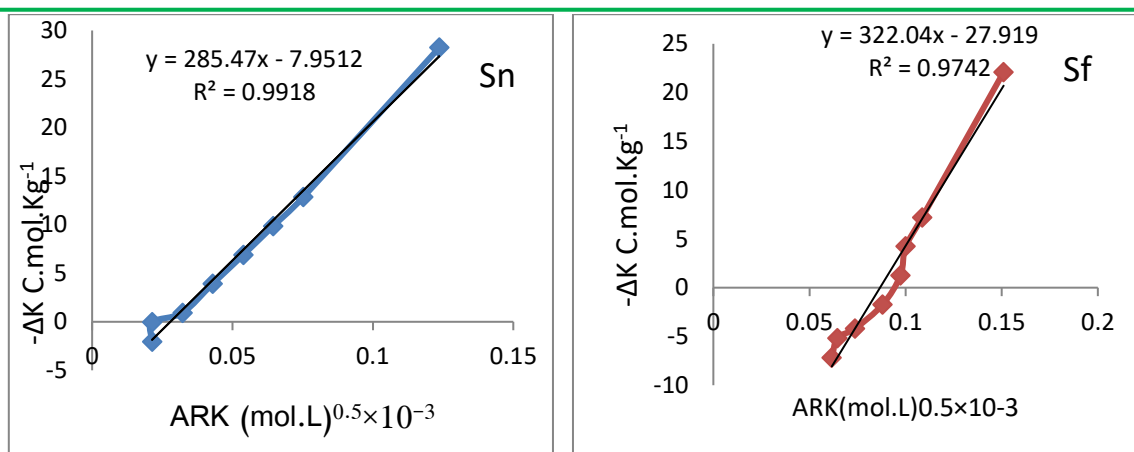
**Table (3): The amount of soluble ions and exchangeable cat ions**

| Potassium forms (Cmol <sub>c</sub> kg <sup>-1</sup> ) |                      |                       |        |         |       |
|-------------------------------------------------------|----------------------|-----------------------|--------|---------|-------|
| Water sol                                             | Ex-CaCl <sub>2</sub> | Ex-NH <sub>4</sub> Cl | Non Ex | Mineral | Total |
| (Baweza – Mosul Aridisol before burning)              |                      |                       |        |         |       |
| 0.020                                                 | 0.20                 | 1.53                  | 2.55   | 5.36    | 7.91  |
| (Baweza – Mosul Aridisol After burning)               |                      |                       |        |         |       |
| 0.100                                                 | 0.72                 | 5.11                  | 8.43   | 0.77    | 9.20  |
| Zawita- Dohok- Mollisols Forests soil before burning  |                      |                       |        |         |       |
| 0.020                                                 | 0.26                 | 2.55                  | 3.06   | 3.58    | 6.64  |
| Zawita- Dohok- Mollisols Forests soil After burning   |                      |                       |        |         |       |
| 0.025                                                 | 0.41                 | 3.06                  | 4.09   | 5.63    | 7.72  |

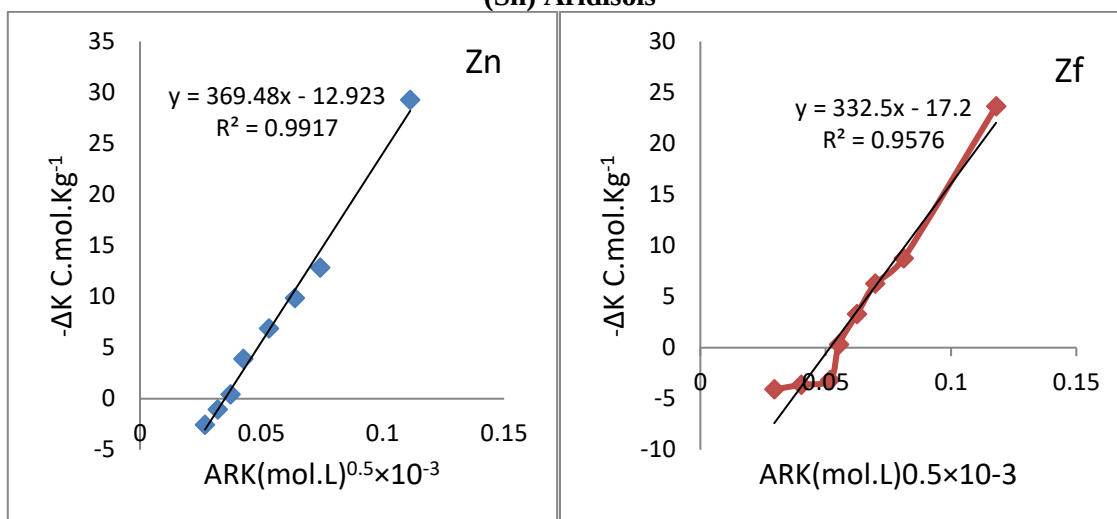
### **Isotherm adsorption (Quantity-to-intensity (Q/I) relationships)**

Figures (1) and (2) show the clear effect of the burning temperature on the behavior of the path and slope of the intensity and quantity relationships Q/I for potassium ion, which is a characteristic of each soil to describe the dynamics of its adsorption and release, which reflects the difference in the organizational capacity of the soil on the supply of potassium, through (Beckett, 1964) on the availability of potassium with graphic relationships called quantity-intensity curves Q/I derived from Gapon equation, 1933) where the linear part of the quantity and intensity curves is proportional to Gapon's coefficient of preference. On the exchange capacity of cations, this constant will be expressed (Sposito, 1977; Evanglou and others, 1994). It is clear from these figures that the soils differ in the values of their slope coefficient and intercept values, and this is related to the difference in texture, mineral composition and soil content of different potassium forms on the one hand, and the effect of fires on Also, the upper part of the curves, which is linear, allows the estimation of the effectiveness ratio of potassium at the equilibrium AR<sub>Ke</sub>, and through it, it is possible to know the adsorption site, whether it is superficial or within the layers, as well as the ability soils to regulate against potassium depletion which was derived from these curves.

. It is also clear from Figures (1) and (2) that the straight part in it expresses the exchanged potassium that is released from release sites easily.. As for the curved part, it clearly indicates the potassium liberated from the more strongly held sites, and these sites are called specialized sites (Specific (Biliias, 2019). The Q/I plots showed a linear relationship at high activity ratios and curvilinear at low- intensity levels, several authors confirm this observation. The slope of the Q/I plot representing a ternary exchange reaction is direct to CEC of the soil (Barbayannis et al.1996; Islam et al. 2017). While Bangroo, et al. (2021) illustrated that the slop of any Q/I plot representing a soil system is a function of CEC,  $k_G$ , and KAR, hence the magnitude of K-loading .The slopes of the plots not only depended on CEC but also on  $k_G$  at low K surface coverage (Where the slopes equated to  $PBC^K$ ).The absence of curvature in the lower portion of Q/I plot is the major difference found by (Al-Hamandi et al.2019). It is not clear why this curvature is absent. None the less, the following hypothesize can be drawn: 1-Since  $K^+$  exchange coefficient was found to be independent of calcite solubility (Al-Kanani, et al. 1991), it is probable that the interactions between  $K^+$  and soil mineral may have contributed to the relatively high values of exchange coefficient.2-A masking effect produced by a relatively high concentration of exchangeable  $K^+$ . These are possible factors responsible for the discrepancy between our results and those above mentioned authors. Since illite and vermiculite constituted between 5-20% of the silica clay content respectively (Al- Kanani et al. 1991; Rasul 2021) of these calcareous soils.



**Figure (1): Q/I relationship of potassium intensity and capacity at Ba'wiza burned (Sf) and unburned (Sn) Aridisols**



**Figure (2): Q/I relationship of potassium intensity and capacity at Zaweta Mollisols in burned (Zf) and unburned (Zn)**

The  $K^+$  - soil mineral interactions may indeed be contributing factors to these linear graphs. These plots show also the relation between quantity factor as a function to intensity factor (KAR) (chemical potential) for labile K compared to the chemical potential of  $Ca^{2+}$  and  $Mg^{2+}$  ions that move to soil solution (Taalab, et.al. (2019)). The plots refer clearly to the variation of values of slopes and intercept this variation due to the variation in chemical, physical and mineralogical properties of soils (Jalali, M., 2007; Rasul, 2021). The upper parts of these plots are linear and also allow determining  $ARK_0$  and soil buffering for K saturation. Also linear parts of plots refer to exchange K that will be release from readily available sites while the curve part of these plots will be from sites that hold extremely (specific sites) (Wang et al., 2004; Joycely, et al. 2018; Kucher, 2018; Kassa, and Kebede, 2019).

#### **Equilibrium activity ratio $AR^{K_e}$ :-**

The  $AR^{K_e}$  value is a gauge of how much labile K is present in soil (Rupa et al. 2003; Lalitha and Dhakshinamoorthy, 2015). From the equilibrated samples, the value of  $AR^{K_e}$  is computed. With a mean value of  $0.035 \text{ (mol L}^{-1}\text{)}$ , the amount of  $AR^{K_e}$  in (Table 3) varied greatly from 0.0279 to  $0.0867 \text{ (mol L}^{-1}\text{)}$ , the findings of the current investigation concur with those of Al-Obaidi et,al (2019) and Al-Hamandi et,al (2019).

The results are shown in figure (1) indicate that the values  $AR^{K_e}$  express the potassium intensity in the soil liquid phase when no potassium gain or loss occurs in the soil and that the adsorption process in these soils does not include surface adsorption on the surfaces of particles Soil only, but it is accompanied by slower stabilization processes between layers of clay (Bourg and Sposito, 2012) and this is consistent with what was found by (Biliyas, 2019) that the interaction of potassium

with soil components includes an initial adsorption reaction (Initial adsorption), it recorded the lowest value of ionic activity  $0.020 \text{ (mol.L}^{-1})^{0.5}$  for Baweza (Aridisols).

**Table (4): The amount of. Potassium parameters driven from Q/I relationships**

| Potassium parameters driven from Q/I relationships   |                                          |                                                                                       |                                       |                                                 |                              |
|------------------------------------------------------|------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------|-------------------------------------------------|------------------------------|
| $AR_e^K$<br>( $\text{mol L}^{-1}$ ) <sup>1/2</sup>   | $L_K$<br>$\text{cmol}_c \text{ kg}^{-1}$ | $PBC^K$<br>$\text{cmol}_c \text{ kg}^{-1}$<br>( $\text{mol L}^{-1}$ ) <sup>-1/2</sup> | $-\Delta G$<br>$\text{kCal mol}^{-1}$ | $k_G$<br>( $\text{L mol}^{-1}$ ) <sup>1/2</sup> | PF<br>Preferential<br>Factor |
| (Baweza – Mosul Aridisols before burning)            |                                          |                                                                                       |                                       |                                                 |                              |
| 0.027                                                | 7.95                                     | 285.47                                                                                | -4819.8                               | 8.45                                            | 0.018                        |
| (Baweza – Mosul Aridisols After burning)             |                                          |                                                                                       |                                       |                                                 |                              |
| 0.086                                                | 27.91                                    | 322.04                                                                                | -3291.4                               | 12.88                                           | 0.019                        |
| Zawita- Dohok- Mollisols Forests soil before burning |                                          |                                                                                       |                                       |                                                 |                              |
| 0.035                                                | 12.92                                    | 369.48                                                                                | -4513.2                               | 8.44                                            | 0.013                        |
| Zawita- Dohok- Mollisols Forests soil After burning  |                                          |                                                                                       |                                       |                                                 |                              |
| 0.051                                                | 17.20                                    | 332.50                                                                                | -3986.4                               | 9.85                                            | 0.025                        |

The present study's findings provide additional evidence that the  $AR_e^K$  regulates the interchange of K ions from the exchange complex to solution phase by indicating the state of the immediately accessible K. (Jalali, 2007). According to IPI (2016) theorized when  $AR_e^K < 0.01 \text{ (mol L}^{-1})^{1/2}$ , it suggests the predominance of K adsorbed to edge sites, whereas  $AR_e^K > 0.01 \text{ (mol L}^{-1})^{1/2}$ , indicates a predominance of K adsorbed to planar positions it is interesting that in no field was  $AR_e^K < 0.001 \text{ (mol L}^{-1})^{1/2}$  which is an indication of K adsorbed to interlattice position. Furthermore, the variation in K adsorption sites in the soils seems to clarify why exchangeable K was a poor predictor of K intensity. In this respect Woodruff (1955) stated that  $AR_e^K$  should be in range at  $2.7 \times 10^{-3}$  to  $34 \times 10^{-3} \text{ (mol L}^{-1})^{1/2}$  in order to have balanced potassium While the highest value of  $0.5 \text{ mol.l}^{-1}$  was recorded (0.04) for the location of Zawytah (Mollisols). The reason may be due to the difference in texture, quantity and type of clay (Bourg and Sposito, 2012) at a temperature of  $298^\circ \text{ K}$ , with a general average of  $0.5 \text{ mol.l}^{-1}$  ( $030 \times 10^{-3}$ ). This indicates that the adsorption in the study soils obtained at the surface positions of the solid phase surfaces between (Planar Positions) (Hamid and Amin, 2017), indicating that the values of the ionic activity ratios of potassium less than  $(0.5-0.01) \text{ mol.l}^{-1}$  indicate the dominance of Adsorption on (Edge site) while values greater than 0.01 indicate the dominance of adsorption on (Planar Positions), which leads us to the conclusion that the process of fertilizing these soils with potassium will expose it to an adsorption process on these sites, which makes it average readiness during the agricultural season. Also, these values are a measure of the instantaneous content of the soil and indicate the intensity of potassium in the liquid soil phase and not the ability to supply it over a long period of time. 0.08 (mol for the Ba'wira site  $0.5 \text{ (l-1. 0.05 (mol for the mol.l-1 angle site) (065} \times 10^{-3}$ ), which reflects the different physicochemical properties of the two sites, which led to the transformation of potassium adsorbed from the (Edge site) to (Planar Positions), which leads us to the conclusion that the process of fertilizing these soils will be easy.

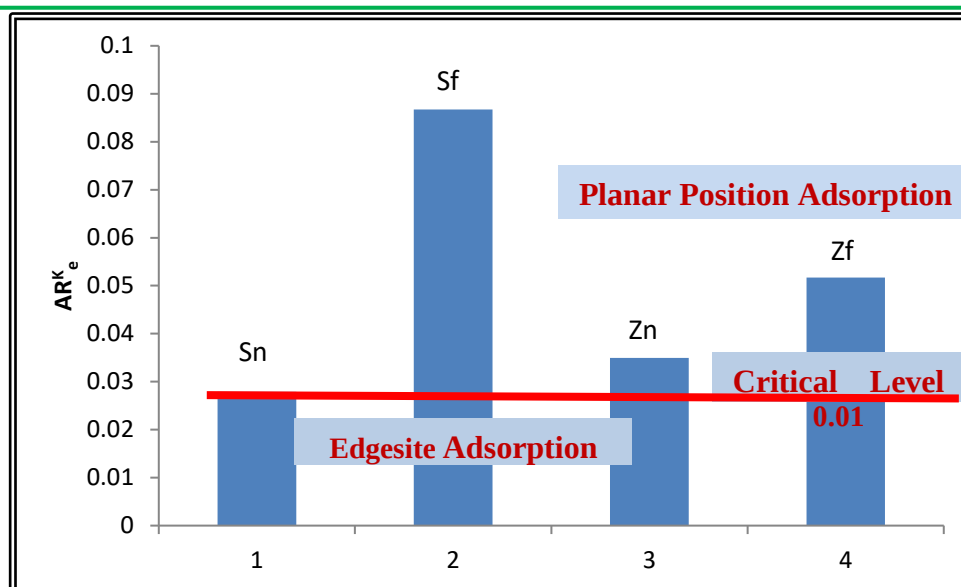


Figure (3): shows the effect of burning on the exchange sites based on the values of the ionic activity ratio of the two study soils before and after burning

### Labile pool of K ( $K_L$ )

The results shown in Table (2) show that the values of unstable space potassium ranged from (7.95Cmolc.Kg-1) for Aridisols (Ba'wiza) site, which rose after burning to (27.91), which is equivalent to 23.6% before burning and 111.6% after burning from the exchange capacity and from (12.92) Cmolc.Kg-1 to (17.2) Cmolc.Kg-1 for the location of Zawytah equivalent to (29.5) % before burning and (51) % after burning of the exchange capacity of the soil. This behavior is related to the mineral composition, both quantitatively and qualitatively, as this value represents the amount of potassium present in the soil. The adsorption surface whose type is Planar Surface( Panda and Patra, 2018), and this can be explained by the fact that the burning processes led to the emergence of new adsorption surfaces that increased the adsorbed potassium and decreased the potassium of the liquid phase (Parlak, 2022). These values also express the potassium associated with non-specialized sites. The high release of potassium to the soil liquid phase, in contrast to the low values, represents soils that contain a limited number of adsorption sites, which makes them characterized by high activity. The potassium associated with the edges is difficult to extract under these conditions. The high values of mobile potassium give a measure of its bound quantity. In non-specialized sites, it also means the high release of potassium to the liquid soil phase, and that soils that contain a limited number of adsorption sites are characterized by high activity, so the clay minerals of soils contribute to an increase in the number of specialized and non-specialized sites responsible for the adsorption of potassium and holding it on the adsorption surface, meaning that the soil Soft soils, which have a high adsorption capacity, need more potassium to provide the plant with the amount required for its growth, while coarse soils need a smaller amount of potassium to reach the highest dissolved concentration in the soil solution, despite not having sufficient reserves to provide the plant with the required amount during the growth period. This represents the amount of K which is capable of ion exchange during the period of equilibration between soil solids and soil solution (Rupa et al., 2003). The labile K ( $K_L$ ) comprises two distinct components, namely the nonspecifically held or immediate source of available K ( $\Delta K_0$ ) and specifically held or difficultly available K ( $K_x$ ) (Rupa et al., 2003; Samadi, 2012). (Najafi-Ghiri and Hamid, 2020) . According to IPI (2016), the critical level of labile K( $K_L$ ) is 2 cmol kg<sup>-1</sup>. The results of the present study are agreed with Rahi et al., 1987. Al-Jumaily, et al(2022) in some soils in Iraq. This clearly indicates that burned soil has a higher potential to replenish the K concentration in the soil solution for a longer period.

### Potential buffering capacity ( $PBC^K$ )

It is noted from Table (2) that the lowest value for the regulatory capacitance of the potassium potential (285.47) was recorded at the Ba'wiza site, while the highest value was recorded at the site of its angle (369.48) at a temperature of  $298\text{ K. kg}^{-1}/\text{mol.l}^{-0.5}$ . As for the burning processes that affected the two sites, it led to an increase in the values of the potassium potential regulatory capacitance values for the Ba'wiza site (322.04), it was reduced in its angle site to 332.50, which reflects the different physicochemical properties of the two sites. This is attributed to the difference in the number of specialized adsorption sites in soils and their ability to hold and adsorption of potassium. The high values of the regulatory capacity of the potassium stress express a stable readiness for potassium for a long period, in contrast to its low values, which gives a clear indication that it needs potassium fertilization at close intervals, which makes these values a criterion for the ability of the soil to maintain the potassium effort against any process of potassium depletion from The liquid and solid phases of the soil. Although the speed of liberation of this element from the non-reciprocal phase to the reciprocal phase cannot be measured from amplitude and strength relations, it is possible to measure the ability of the soil to maintain the change that occurs to potassium, which makes it give an indicator of liberation (Islam et al., 2017 ; Hamid and Amine, 2017).

The potential buffering capacity ( $PBC^K$ ) equal to the amount of labile K can be removed before  $AR^{K_e}$  falls by more than given a mount, it was calculate as the slope of the linear portion of the Q/I curve ( $\Delta Q/\Delta I$ ).The straight line section of Q/I plot in the figures represents the linear buffering capacity ( $PBC^K$ ) of the soils, which is a measure of the ability of the soil to maintain the intensity of K in soil solution Samadi, (2012).The  $PBC^K$  values are indicative of soil capacity for maintaining a given K activity (concentration) at equilibrium conditions in case of K uptake by plants or leaching (Wang et al. 2004). The  $PBC^K$  values of the studied soils prove to be of much help in explaining the limiting validity of the equilibrated ratio values in describing the potassium status of many of the studied soils .The  $PBC^K$  values as shown in Table (3) refer to that all studied soil poorly K-buffered. This can be attributed to their high content in  $\text{CaCO}_3$  equivalent after afire, the value of this K-parameter ranged between  $42.53\text{ cmol kg}^{-1} (\text{mol L}^{-1})^{-1/2}$  in the soil and  $92.42\text{ cmol kg}^{-1}(\text{mol L}^{-1})^{-1/2}$  in the, with a mean  $66.03\text{ cmol kg}^{-1} (\text{mol L}^{-1})^{-1/2}$ . Soils with the ahighest  $PBC^K$  value were characterized by the lowest percent K saturation, indicative of higher potential to replenish K concentration in soil solution High  $PBC^K$  values are a measure of constant availability of K in the soil solution over a long period, whereas low  $PBC^K$  would suggest the need for frequent K supply throughout fertilization practice

### Gapon Selectivity Coefficient ( $k_G$ )

It is noted from Table (2) that the values of Gapon Selectivity Coefficient ( $k_G$ ) were close in the two locations before the fires (8.45) and (8.44)  $\text{L.mol}^{-0.5}$  hit them. At the sites of Baweza and Zawita, respectively. As for the burning operations that affected the two sites, it led to an increase in the Gapon constant for the Bawerah site to 12.88, with an increase of 52%, and in the Zawiya site, it increased to (9.85) and with an increase of 17%. A new exchange as a result of fires, and then the value of the preference Gapon Selectivity Coefficient ( $k_G$ ) increases, and this is consistent with what was indicated by Ulery et al., (2017) There is a decrease in the ion exchange capacity of many soils that have been burned, as the burning of dense vegetation exposes the base soil to high temperatures, which causes the occurrence of Thermal change in soil minerals and other changes in soil properties. This was confirmed by the values of Gapon Selectivity Coefficient ( $k_G$ ) of preference, which indicated that the potassium present on the surface of the colloids is of the type bound to the edges, as potassium is characterized by being the largest positive ion in its non-diagonal state among plant nutrients with a radius of  $1.33^\circ\text{A}$  and a harmonic number 8-12. Potassium is characterized by a relatively high selectivity In its ionic interaction in soil, it has a high polarity ( $142.5\text{ kJ.g}^{-1}$ ) compared to other nutrients.The Gapon selectivity coefficient for K expresses the relative affinity soils may develop towards K in the presence of Ca and Mg both in the soil solid phase and soil solution under equilibrium conditions. Most of the  $k_G$  values fluctuated within the range 8.44 to 12.88  $(\text{L mole}^{-1})^{1/2}$ , suggesting that the relative affinity for K was quite

similar (Table 3). The changes in  $k_G$  values are basically attributable to the levels of exchangeable Ca and Mg Bernard et al. (2006). Soil selective behavior for K in comparison with dominant Ca and Mg may also be attributed to the preferential attraction of K ions over Ca and Mg (Najafi-Ghiri and Abtahi, 2012) at some planar sites of soil colloids, if  $Ca_{ex} + Mg_{ex} \approx CEC$  is assumed. The preferential factor  $PF = \frac{K_{ex}}{(Ca + Mg)_{ex}}$  values (Table 3) varied between 0.007 and 0.03 indicating that soils have generally exhibited a quite similar preference for potassium. On the basis of (Bernard et al., 2006) soils have  $PF < 0.100$  characterized by higher soils preference for Ca and Mg over K in contrast to soil have  $PF > 0.100$ , where K seems to be more preferentially attracted. The results indicate a higher preference for Ca and Mg over K.

#### Fertility assessment of burned soils

The indicator of AR for potassium was used with logarithmic values, which express the values of potassium potential in terms of the negative logarithm of  $AR_{Ke}$  for the liquid phase of soil when there is no gain or loss of potassium in the soil after the thermodynamic equilibrium process for these soils without adding any potassium level, which is shown in Figure (4). The value of the potassium potential ranged from (4.698) for the unburned Ba'wiza soil site to (4.397) for the unburned Zawita site, while the fires that affected the two sites led to an increase in the value of the potassium potential, as its value reached (4.096) at the Ba'wiza site (4,096) and the Zawita site (4.301). According to the classification proposed by the scientist Woodruff, 1955) in determining the potassium potential in the soil, he indicated that the potassium potential of greater or equal to (2.75) is in soils that suffer from a lack of potassium supply, and the preparation is appropriate and good when the potassium effort reaches (2.20). And when it drops below (1.47), there will be an increase in potassium supply, so the study soil is less than the critical limit (2.75), which makes the study soil suffer from a lack of potassium supply. The fertility is classified as medium to poor, and this may be due to the soil minerals responsible for stabilizing potassium (elite) (Kenya, 2013). Figure (4) Minerals controlling solubility and decreasing its release in addition to the high pH values to the neutral neutrality in the middle of the equilibrium with the role of For carbonate minerals in this regard, the values of equal intensity do not have an equal regulatory capacity in order to maintain the soil during the period of depletion of this element by plant roots (Hamid and Amine, 2017).

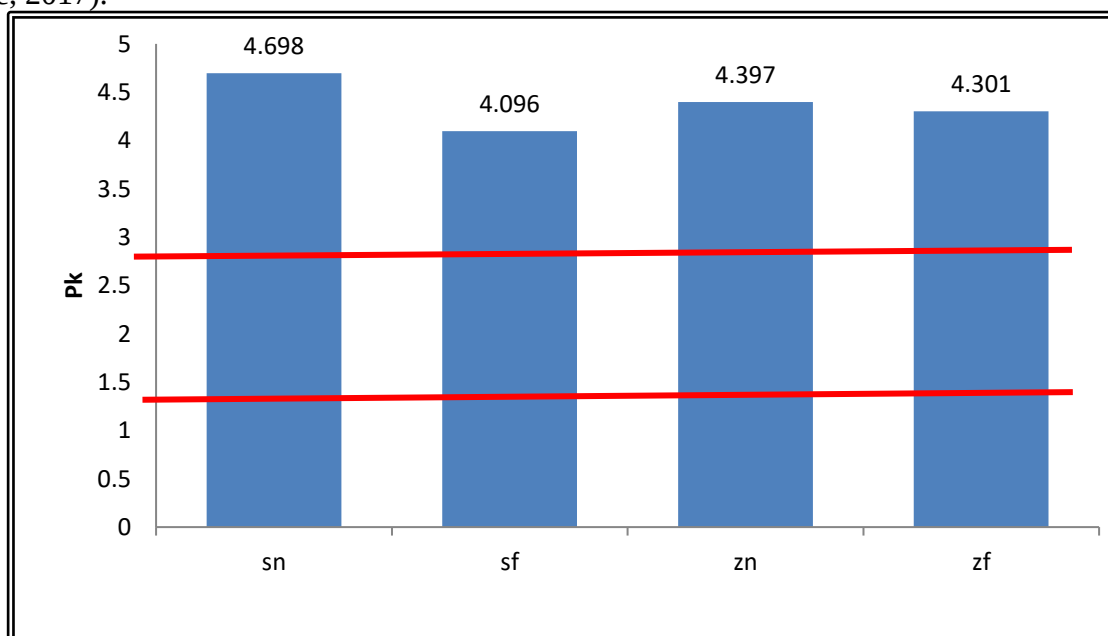


Figure (4): Potassium potential values for the two study soils before and after burning

#### Free energies of exchange of Ca with K ( $-\Delta G$ ):

The results shown in Figure (5) indicate the free energy values for the thermodynamic equilibrium state at a temperature of 298 K, which express the energy changes caused by physical and chemical adsorption reactions (Woodruff, 1955). This energy is a more comprehensive thermodynamic function to detect the spontaneity of the reaction because it represents the sum of two factors (the

change in heat capacity and the factor of change in the randomness of the reaction) and the free energy is calculated based on the values of the equilibrium constant  $AR^{K_e}$  for ratios to the ionic activity of potassium when there is no gain or loss of potassium. The reaction spontaneously ranged from (4819.8) Calory/mol/Kelvin at the Ba'wiza site to (4513.3) Calory/mol/Kelvin at the Zawiya forest site Calory/mol/Kelvin. As for the burning processes that affected the two sites, it led to an increase in the free energy values (3291.64) Calory/mol/Kelvin in Baweza site to (4513.3) Calory/mol/Kelvin in Zawita Forest Calory/mol/Kelvin The change in the free energy values between the soils is directly related to the change in the equilibrium conditions of the soil solution with its solid phase, and the results we obtained It agrees with what was obtained by Sparks and Liebhart (1981), who indicated the type of minerals present in the soil and temperature changes will affect the effectiveness of ions in the soil liquid phase, and the results are shown in the table indicate that all energy values The free equilibrium solution is negative, which indicates the spontaneity of the thermodynamic reaction. It was also used as an indicator of potassium readiness according to Lalitha and Dhakshinamoorthy (2015), as figure (5) shows that the soils of Ba'wiza and Zawiya suffer from a lack of potassium supply, and that the fires that affected the two sites led to the ease of releasing and supplying potassium to the soil solution. Free energy of exchange ( $-\Delta G$ ), represented by the term  $RT \ln AR^{K_e}$ , is related to one chemical equivalent of potassium in the standard state replacing one chemical equivalent of calcium on clay followed by the liberation of certain calories or joules of energy (Rupa et al. 2003). A mount of ( $-\Delta G$ ) was varied between two soils and after burning,.According to the standard for  $-\Delta G^{K_e}$  reported by Woodruff (1955), the K supply for all soils is relatively high (i.e.  $-\Delta G^{K_e}$  less than  $-0.6 \text{ k J mole}^{-1}$ , basically). As stated by (Roy et al., 1991), soils with higher exchangeable K (%K saturation) were generally characterized by low  $-\Delta G^{K_e}$  values.

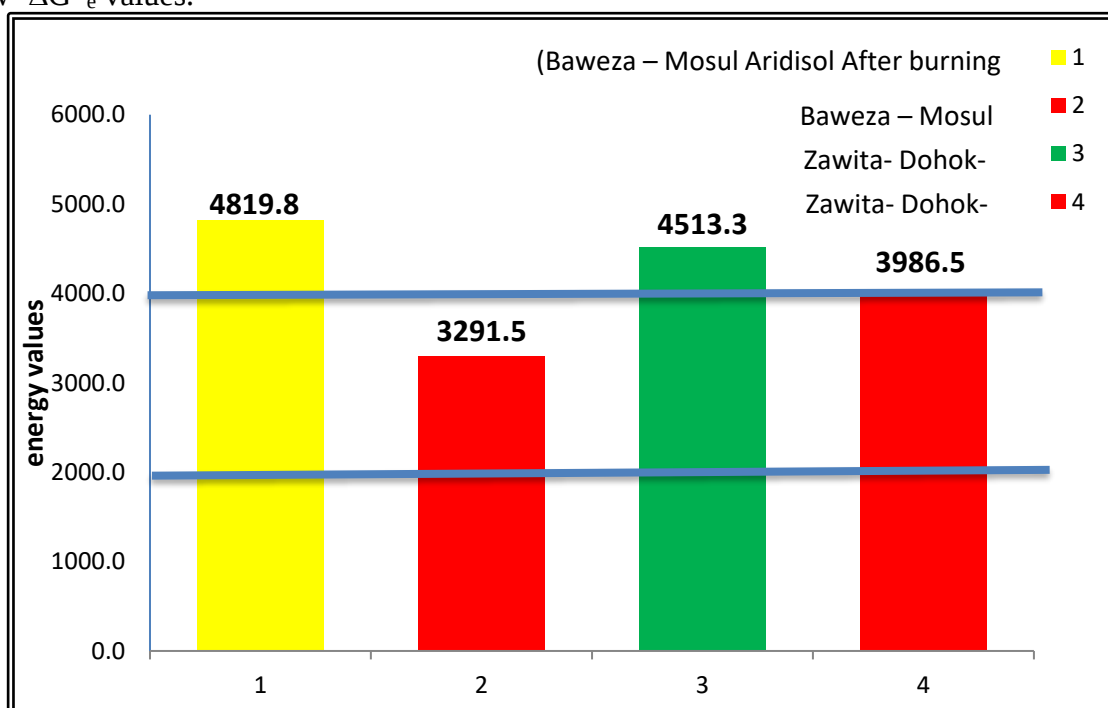


Figure (5): Fertility evaluation of the study soils according to the free energy values of potassium for the two study soils before and after burning

## CONCLUSION

The burning processes that have signed the two sites caused a great affection on potassium availability to be more available and may be lost by leaching deeply .thus need espials management in these soils.

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## السعة التنظيمية لجهد البوتاسيوم في بعض الترب المحروقة شمالي العراق

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### الخلاصة

تم إجراء هذا البحث لدراسة السلوك السعة التنظيمية لجهد البوتاسيوم لترب تعرضت الى الحرق في رتبة التربة Aridsol في موقع بعويزة والمشهورة بزراعة الحبوب ضمن الموقع الجغرافي وموقع غابات زاوية ضمن رتبة التربة Mollisols في محافظة دهوك في شمال العراق. لدراسة تأثير الحرق السعة التنظيمية لجهد البوتاسيوم باستخدام مدخل الديناميك الحراري وفقاً لعلاقة الشدة و الكمية (Q / I) عند K298 o وقد اشارت النتائج الى الاثر الكبير لعمليات الحرق الى تحول كبير في جاهزية البوتاسيوم بكافة معايير وبالتالي امكانية خسارته بالغسل الى اعماق التربة فقد تراوحت قيمة ARKe بشكل كبير من 0,02 إلى 0,08 لتر.مول 0,5 ، يتراوح البوتاسيوم القابل للتحرر (LK) من 7,951 إلى 27,919 سنتيمول شحنة كغم-1، وتراوحت السعة التنظيمية لجهد البوتاسيوم (PBCK) بين 285,47 و 369,48 سنتيمول شحنة كغم-1، وتراوحت قيم الطاقة الحرة للتبادل (G-) بين 3291,8 و 4819,8 سرعة.مول-1 وتراوحت قيم معامل التفضيل لكابون (kG) من 8,44 إلى 12,88 (لتر.مول-1) 2/1 . كانت قيم PF من 0,018 إلى 0,025 .

### الكلمات المفتاحية:

السعة التنظيمية للبوتاسيوم ،  
الترب المحروقة ، الترب الكلسية  
، الموصل، دهوك