

Non-Isothermal Decomposition of Al, Cr and Fe Cross-Linked Trivalent Metal-Alginate Complexes

Ishaq A. Zaafarany

*Chemistry Department, Faculty of Applied Sciences,
Umm Al-Qura University, Makkah, Saudi Arabia*

ishaq@uqu.edu.sa

Abstract. The thermal decomposition of Al^{III} , Cr^{III} and Fe^{III} metal-alginate complexes have been investigated thermogravimetrically using (TG) and (DTG) techniques in static air. However, the TG curves showed three stages of weight loss, the DTG curves indicated the presence of a series of thermal peaks associated with the TG curves. The thermal dehydration of the coordinated water molecules was found to occur in the first stage, whereas the decomposition of the dehydrated complexes occurred in the second and third stages, respectively. The results revealed the formation of hydroxide, oxalate and carbonate for Al^{III} , Cr^{III} and Fe^{III} metal-alginate complexes, respectively, followed by decomposition of these intermediate fragments to the corresponding metal oxides as final products. These complexes have been characterized by FTIR and chemical analysis. A tentative mechanism for decomposition has been suggested and discussed in terms of the strength of chelation and the structure geometry.

Introduction

Alginate is a polyelectrolyte which consists of a binary heteropolymer consisting of 1,4 linked β -D-mannuronic and α -L-guluronic acid units in a linear block copolymer structure.^[1-4]

The thermal decomposition of solid materials proceeded in two directions, using either the powdered material or a single crystal. The former studies are much more extensive than the latter one. The advantages of the solid state decomposition were attributed to the destruction of the crystal lattice of the sample, the breaking

and redistribution of the chemical bonds involved, the formation of the crystal lattice of the product and the diffusion process of one component or the other through the product layer for further propagation of the dissociation reactions.^[5]

Although, there are some reports on the thermal decomposition of some cross-linked divalent and hexavalent metal-alginate complexes,^[6-9] it seems that no attempt has been made with respect to alginate complexes of trivalent metal ions. Therefore, the present work is of great significance to shed some light on the thermal decomposition of these complexes as well as to gain some information on their chemical stabilities compared with that of other polyvalent metal-alginate complexes. Again, since trivalent metal-alginate complexes possess electrical properties lie in the range of semiconductors, they can be applied in some solar energy cells and electrical devices.

Experimental

All materials used were of Analar quality (BDH). Metal-alginates in the form of granules were prepared by replacement of Na^+ counter ions of alginate macromolecule by Al^{3+} , Cr^{3+} and Fe^{3+} metal ions. This process was carried out by stepwise addition of the alginate powder reagent to electrolyte solutions of these metal ions (Ca. 1.0M) whilst stirring the solutions vigorously in order to avoid the formation of lumpy gelatinous precipitate of metal-alginate gels which swell with difficulty. After completion of exchange processes, the metal-alginate granules formed were washed with deionized water several times, then with doubly distilled water until the washings become free from the metal ions. The sample complexes were dried at about 105°C under vacuum over anhydrous CaCl_2 or P_2O_5 .

Thermogravimetry (TG) and differential thermogravimetry (DTG) analyses were carried out using a Mettler TA 3000 thermal analyzer in static air, the heating rate was 10 K min^{-1} in static air.

FTIR spectra were recorded on a Pye Unicam Sp 3100 spectrophotometer using the KBr disc technique ($4000\text{--}200\text{ cm}^{-1}$). The vibration assignments of the bands are shown in Fig. 1.

The microanalyses were performed with a microanalyzer and the analytical data of the complexes are presented in Table 1.

Table 1. Analytical Data for Metal Alginate Complexes.

Complex	Found (%)			Calculated (%)			Formula
	C	H	M	C	H	M	
Al^{III} -alginate	35.89	4.56	4.31	35.53	4.77	4.44	$\text{C}_{18}\text{H}_{21}\text{O}_{17}\text{Al} \cdot 4\text{ H}_2\text{O}$
Cr^{III} -alginate	34.33	4.55	8.24	34.12	4.58	8.21	$\text{C}_{18}\text{H}_{21}\text{O}_{17}\text{Cr} \cdot 4\text{ H}_2\text{O}$
Fe^{III} -alginate	33.82	4.41	8.88	33.92	4.55	8.74	$\text{C}_{18}\text{H}_{21}\text{O}_{17}\text{Fe} \cdot 4\text{ H}_2\text{O}$

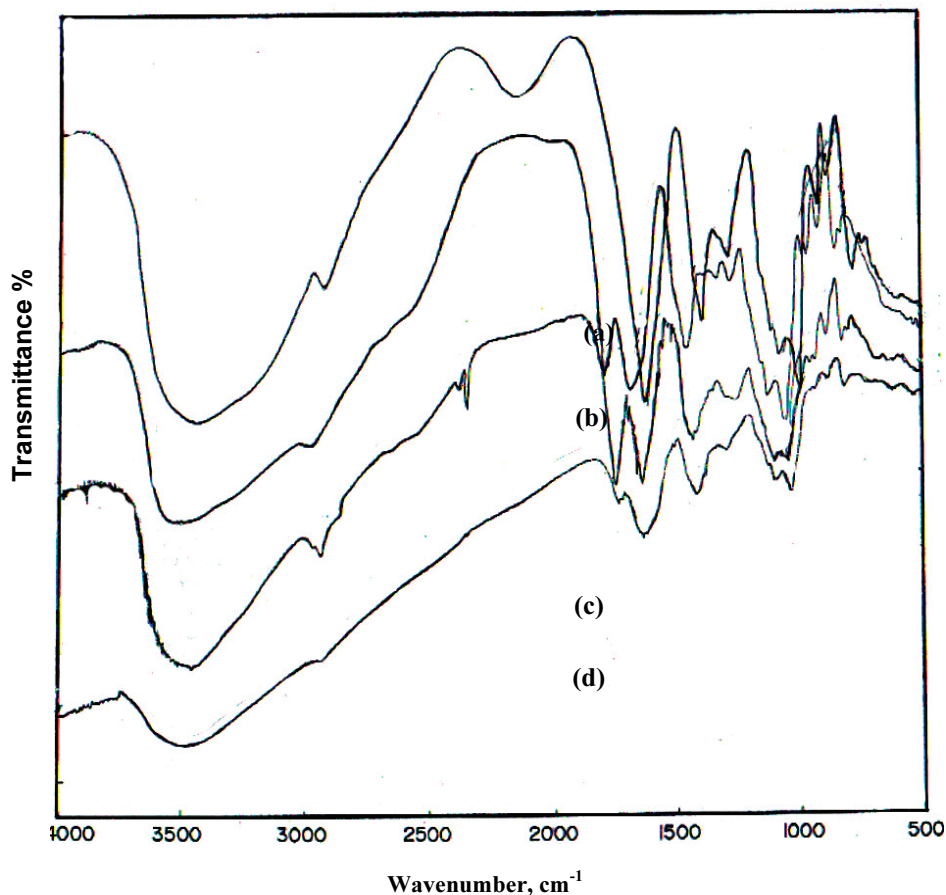
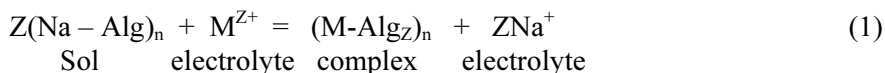


Fig. 1. Infrared spectrum of (a) sodium alginate, (b) cross-linked aluminum (III)-alginate complex, (c) cross-linked iron(III)-alginate complex and (d) cross-linked chromium (III)-alginate complex.

Results and Discussion

The replacement of Na^+ counter ions of alginate macromolecule by polyvalent metal ions of the electrolyte solutions can be expressed by the following stoichiometric equation



where M denotes the metal ion and Z stands to its valency. Any counter ions which leave the macromolecular chains of alginate must be compensated by an equivalent amount of other metal ions, even if the mobilities and valencies of

the two counter ions are quite different.^[10-12] This is the necessary demand of electroneutrality. The exchange processes for the formation of the complexes studied were found to be inherent stoichiometrically.^[13-16]

The infrared spectra of the present complexes have been measured and the vibration assignments of the bands are cited in Table 2. It is well known^[17] that the bands correspond to the symmetry stretching vibrations of the $-\text{OCO}-$ (ν_s) in sodium alginate lie at 1400 cm^{-1} and that of the asymmetric stretching vibrations (ν_{as}) lie at 1600 cm^{-1} . A broad band is located near 3500 cm^{-1} due to the stretching vibration of the hydrogen bond of water or the hydroxyl group. Again, the free ligand has a strong band in the 1735 cm^{-1} . As shown in Table 2, the band of the stretching vibrations of $-\text{OCO}-$ group is shifted from 1400 cm^{-1} (ν_s) to $1418\text{--}1425\text{ cm}^{-1}$ whereas the band at 1600 cm^{-1} (ν_{as}) is shifted to $1633\text{--}1648\text{ cm}^{-1}$, respectively. This result indicates the participation of $-\text{OCO}-$ groups in the chelation. Again, the shift in the ν_{OH} band to lower frequencies which becomes more broader than that of sodium alginate may also indicate the sharing of OH groups in the chelation process.

Table 2. Infrared frequencies (cm^{-1}) for sodium and metal alginate complexes.

complex	$\nu_{as}\text{OCO}$	$\nu_s\text{OCO}$	ν_{OH}	$\nu_{\text{M-O}}$	Reference
Na-alginate	1600	1400	3500	850	6
Al^{III} -alginate	1648	1425	3490	830	This work
Cr^{III} -alginate	1637	1420	3463	810	This work
Fe^{III} -alginate	1633	1418	3448	817	This work

Furthermore, the model structure of coordination plays an important role in the stability of these metal alginate complexes. Polyvalent metal ions tend to chelate the carboxylate and hydroxyl functional groups of alginate macromolecular chains via either intra- or intermolecular association in order to attain a stable coordination geometry. This depends on the nature, valency and coordination number of the chelated metal ions. Since the divalent metal ions are chelated with two carboxylate groups and one or more pairs of hydroxyl groups of alginate macromolecular chains, the two geometrical structures (intra- and intermolecular associations) are possible in chelation. On the other hand, trivalent metal ions cross-link three carboxylate groups and one or more pairs of the hydroxyl groups depending on the coordination number of the chelated metal ion. Hence, trivalent metal ions are restricted to cross-linking via intermolecular association in their alginate complexes for geometrical reasons. The preferability of the intermolecular association for trivalent metal-alginate complexes may be explained by their tendency to decrease the bond stretching resulting from metal-oxygen bond elongation in case of intramolecular association. This association may explain the weak mechanical properties of trivalent metal alginate complexes in their gel forms, in handling, when compared with those of divalent metal ions.

The thermal decomposition curves of The studied complexes are shown in Fig. 2. The TG curves exhibit three stages of weight loss, the DTG curves indicate the presence of a series of thermal decomposition associated with the TG curves. This behaviour is quite different than that observed in sodium alginate macromolecule,^[6] and may be explained by the difference in the strength of chelation resulting from the partially ionic bonds between sodium and trivalent metal ions with the carboxylate groups as well as the presence of partially coordinate bonds between trivalent metal ions and hydroxyl groups, whereas is not found in sodium-alginate.

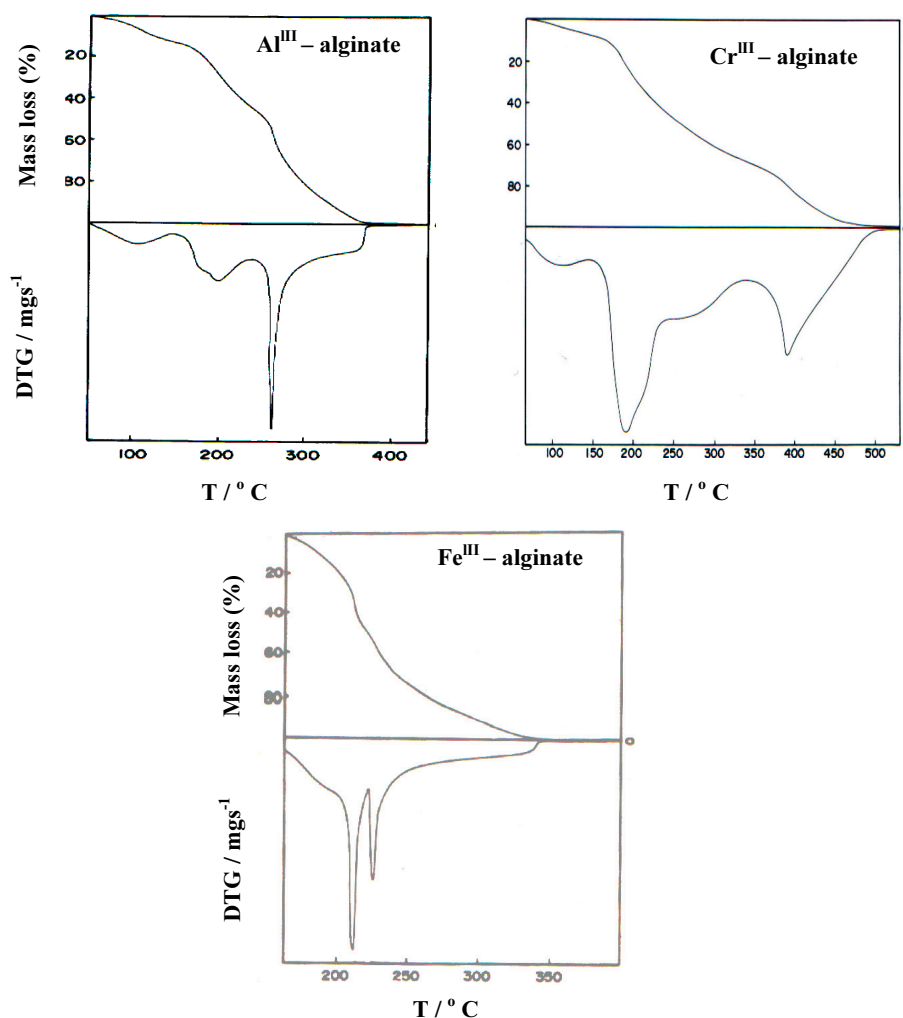
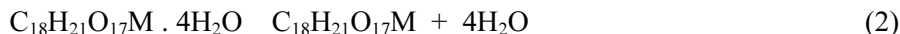
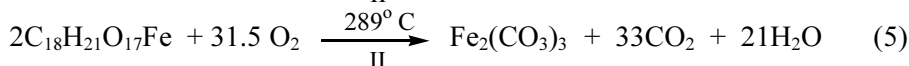
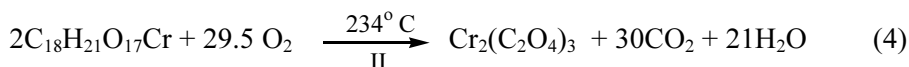


Fig. 2. TG and DTG curves of cross-linked metal-alginate complexes.

In view of the thermal decomposition behaviour of other divalent metal-alginate complexes reported elsewhere,^[6,9] a suitable mechanism of thermal decomposition consistent with the experimental observations may be suggested. The weight loss observed in the first stages in the TG curves (Table 3) can be explained by the evolution of four coordinated water molecules as follows,



The weight losses associated with the second stage (Table 3) were found to be in a good agreement with the calculated weight loss which associated with the decomposition of the metal-hydroxide, oxalate and carbonate in case of Al^{III} , Cr^{III} and Fe^{III} – alginate complexes, respectively. Consequently, the decomposition of these complexes can be expressed by the following equations,



where $\text{C}_{18}\text{H}_{21}\text{O}_{17}$ are three monomers of alginate macromolecules chelated with each trivalent metal ion.

These intermediate fragments are decomposed to give the corresponding metal oxides as final products as follows,

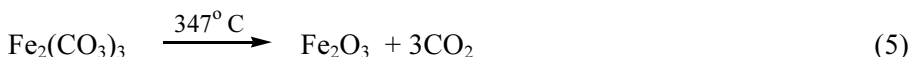
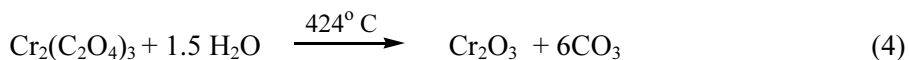
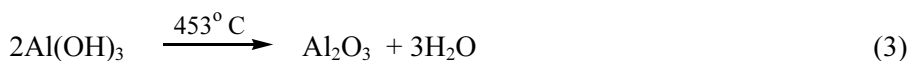
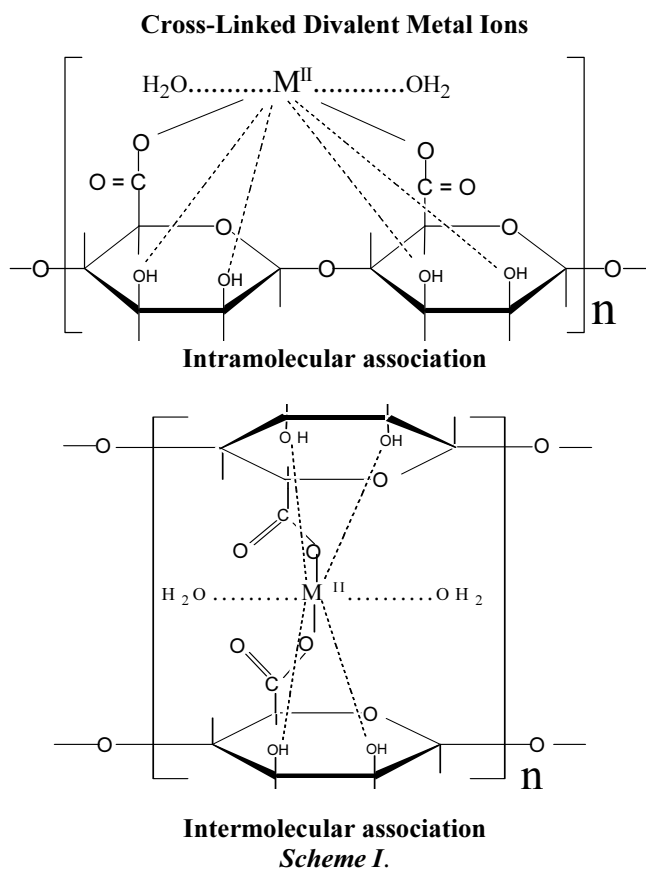


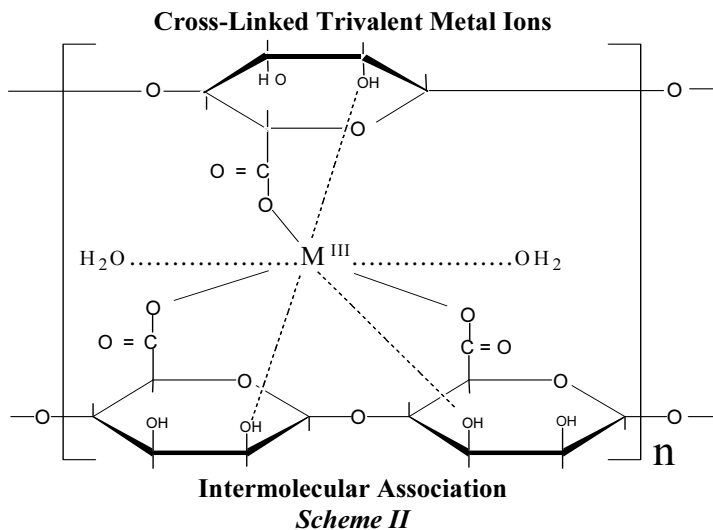
Table 3. The Maximum decomposition (T_{max}) and the weight loss accompanying the stages of decomposition (10 K) min.

Complex	Stage	TG			Weight loss (%)	$T_{\text{max}} / ^\circ \text{C}$
		$T_i / ^\circ \text{C}$	$T_m / ^\circ \text{C}$	$T_f / ^\circ \text{C}$		
Al^{III} -alginate	1 st	53	106	190	12.1	220
	2 nd	190	220	340	52.7	
	3 rd	340	395	453	29.1	
Cr^{III} -alginate	1 st	51	104	151	11.8	210
	2 nd	151	207	234	29.9	
	3 rd	234	234	424	55.5	
Fe^{III} -alginate	1 st	53	101	145	11.2	205
	2 nd	145	205	289	42.2	
	3 rd	289	293	347	43.9	

T_i : initial, T_m : medium and T_f : final

The values of the maximum decomposition temperature of the main process (Table 3) may reflect the stability of the metal-alginate complexes. The observed values indicate that the stability decreases in the order $\text{Al} > \text{Fe} \geq \text{Cr}$ – alginates. The order of stability agrees very well with the magnitude of M-O bond energies,^[18] *i.e.* the stability depends on the strength of chelation between the chelated metal ion and functional groups of alginate macromolecule. In intramolecular association the functional groups involved in chelation are belonging to the same chain. Hence, the plane involving the chelated metal ion is parallel to the plane of alginate macromolecular chains. This configuration may be called a planar geometry. While, in intermolecular association the plane containing the metal ions is perpendicular to the plane of alginate chains and the involved functional groups are related to different chains. Here, the configuration obtained is termed a non-planar geometry.^[19] The two geometrical configuration are shown in Schemes I and II.





Conclusion

The thermal decomposition of Al^{III} -, Cr^{III} - and Fe^{III} - alginate complexes have been studied using thermogravimetry (TG) and differential thermogravimetry (DTG) methods. The experimental observations showed the presence of three stages of weight loss (TG) associated with a series of thermal decomposition (DTG) curves. The first stage was explained by the evolution of four coordinated water molecules for all cited complexes, followed by the decomposition of the dehydrated complexes in the second and third stages. The results revealed the formation of metal hydroxide, oxalate and carbonate for Al^{III} , Cr^{III} and Fe^{III} – alginate complexes followed by decomposition of these intermediate fragments to the corresponding metal oxides as the final products.

References

- [1] Fisher, F.G. and Dorfel, H. (1955) *Z. Physiol. Chem.*, **302**: 186.
- [2] Whistler, R.L. and Kirby, K.W. (1955) *Z. Physiol. Chem.*, **314**: 46.
- [3] Chanda, S.K., Hirst, E.L., Percival, K.G.V. and Koss, A.G. (1952) *J. Chem.Soc.*, : 1833.
- [4] Rees, D.A. (1972) *Biochem. J.*, : 126, 257.
- [5] Mousa, M.A., Summan, A.M. and Al-Sousi, G.N. (1990) *Thermochim. Acta*, **165**: 23.
- [6] Said, A.A. and Hassan, R.M. (1993) *Polym. Degrad. Stabil.*, **39**: 393.
- [7] Said, A.A., Abd El-Wahab, M.M. and Hassan, R.M. (1994) *Thermochim. Acta*, **233**: 13.
- [8] El-Gahami, M.A., Khairou, K.S. and Hassan, R.M. (2003) *Bull. Polym. Acad. Sci.*, **51**: 05, El-Gahami, M.A., Hassan, R.M. and Khairou, K.S., *J. Therm. Anal. Calor.*, (Accepted for publication).
- [9] Khairou, K.S. (2002) *J. Therm. Anal. Calor.*, **69**: 583.

- [10] **Haugh, A.** and **Smidsrod, O.** (1965) *Acta Chem. Scand.*, **19**: 341.
- [11] **El-Shatoury, S.A., Hassan, R.M.** and **Said, A.A.** (1992) *High Perform. Polym.*, **4**: 173.
- [12] **Helfferrich, F.** (1962) "Ion Exchange", McGraw-Hill, New York, p. 250.
- [13] **Hassan, R.M., El-Shatoury, S.A. Mousa, M.A.** and **Hassan, A.** (1988) *Eur. Polym. J.*, **24**: 1173.
- [14] **Hassan, R.M., Summan, A., Hassan, M.K.** and **El-Shatoury, S.A.** (1989) *Eur. Polym. J.*, **25**: 1209.
- [15] **Hassan, R.M.** (1991) *J. Mater. Sci.*, **26**: 5810.
- [16] **Hassan, R.M.** (1991) *J. Mater. Sci.*, **28**: 384.
- [17] **Bellamy, L.J.** (1966) "*The Infrared Spectra of Complex Molecules*", 2nd Ed., p. 354.
- [18] **Sanderson, R.T.** (1976) "*Chemical Bonds and Bond Energy*", 2nd Ed., Academic Press, New York.
- [19] **Hassan, R.M.** (1993) *Polym. Inter.*, **31**: 81.

دراسة التحلل الحراري لمتراكبات الألجينات الفلزية لأيونات الألومينيوم والكروم والحديد الثلاثية التكافؤ باستخدام تقنيات التحلل الحراري الغير معزول

إسحاق عبدالله علي زعفراني

قسم الكيمياء - كلية العلوم - جامعة أم القرى

مكة المكرمة - المملكة العربية السعودية

المستخلص. تم دراسة حركية وميكانيكية التحلل الحراري لمتراكبات الألجينات الفلزية لأيونات الألومينيوم والكروم والحديد الثلاثية التكافؤ باستخدام تقنيات الطرق الحرارية الوزنية (TG) والطرق الحرارية التفاضلية (DTG) في الهواء الجوى. وقد أظهرت نتائج التحلل الحراري الوزني وجود ثلاث مراحل واضحة في معدل النقص في الوزن بينما أظهرت نتائج التحلل الحراري التفاضلي وجود سلسلة من القمم المتداخلة مع منحنيات التحلل الوزني. كما أوضحت النتائج بأن عملية التحلل الحراري لكل متراكب تتم بانطلاق جزيئات ماء التبخر الأربعة في المرحلة الأولى (أقل من ١٩٠ درجة مئوية) يليه تحلل المتراكبات الناتجة الخالية من ماء التبخر في المرحلتين التاليتين حيث تتم في المرحلة الأولى منهما تكون متراكب وسيط هو عبارة عن هيدروكسيد الفلز (من ٢٣٠-٢٣٤ درجة مئوية) يتبعه تحلل هذا الهيدروكسيد إلى أكسيد الفلز في المرحلة الأخيرة كنتاج نهائي (من ٣٤٧-٤٥٣ درجة مئوية). وقد تم حساب الدوال الكيناتيكية باستخدام نماذج متنوعة. وبناء عليه تم وضع ميكانيكية مناسبة لعملية التحلل الحراري والتي تتفق تماما مع النتائج الكيناتيكية.