

THE EFFECT OF THE ANION AND CATION OF THE CATALYST
ON THE CATALYTIC MULLITIZATION OF KAOLINITE

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ABSTRACT

Results are presented of an investigation into the effect of the anion and the cation of various catalytic additives on mullite development in a Georgia Kaolin. The sodium and potassium compounds investigated were found to be poor catalysts. The calcium compounds were very good catalysts while the lithium compounds ranged from poor to very good for lithium chloride. It was found that the catalysis of mullite is affected by the anion although its effect is not as pronounced as that due to the cation.

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I. INTRODUCTION

From a confused beginning at the turn of the century, investigation of the compound "mullite" has given the ceramic industry a great deal of simplified fact and sound theory concerning its structure, formation and behavior.

In 1909, Shepard, Rankin and Wright¹ made a great stride when they established the fact that only one compound of alumina and silica was stable at high temperatures. It remained, however, for Bowen and Greig² to determine its composition as $3Al_2O_3 \cdot 2SiO_2$. These investigators working with Zies³ gave this compound the name Mullite as a result of its discovery in the natural state on the Island of Mull.

Bowen and Greig² were perhaps the first to uncover the possibility of mullite catalysis when they succeeded in growing mullite crystals at $1050^\circ C.$, which could be identified under the microscope, by the addition of various fluxes to alumina-silica mixtures.

A number of investigators have studied this catalytic effect due to foreign materials but, considering the available literature, their work has been concerned primarily with the effect of the cation in the catalyst.

The purpose of this investigation was to determine whether or not the anion of the catalyst plays a part in mullite formation or growth.

II. REVIEW OF LITERATURE

Budnikov and Khizh⁴ observed an increase in mullite development at the zone of contact of a slag high in iron oxide and a refractory brick. In further work, Budnikov⁵ observed that mullite formation was promoted at 1200° to 1350° C. by the addition of iron compounds to clay.

The first comprehensive investigation of mullite catalysis was probably the work done by Yoshioaka and Isomatsu⁶. They added 1% flux to a clay and heated the samples for one hour at 1400° C. These samples were crushed through a 200 mesh sieve and digested for six hours in a hydrofluoric acid solution at 0° C. after ascertaining that quartz and fused silica are almost completely dissolved and that mullite is attacked to a limited degree under these conditions. The effectiveness of the additions they made, in order of decreasing mullite yield, were as follows; boric oxide, ferric oxide, steatite, talc, orthoclase, calcium oxide and calcium fluoride.

Nakai and Fukasi⁷ using X-ray diffraction techniques made a study of the effect of 0.5, 2 and 5% additions of mineralizers to kaolin, a kaolin-alumina mixture, and a quartz-alumina mixture. They found that lime, lithia, sodium tungstate, calcium oxide, magnesia, bismuth subnitrate, litharge, ammonium molybdate, boron oxide, manganese dioxide and cupric oxide were effective mineralizers. In every case the temperature of mullite formation was lowered 50° to 200° C. and each mineralizer seemed to have a temperature at which it was most effective.

Farmelee and Rodriguez⁸, using hydrofluoric acid and X-ray methods, found that the oxides of zinc, lithium, magnesium, iron, manganese, cerium and molybdenum were good mullite formers, whereas, sodium, potassium, titanium, and stannic oxides were poor, and boric

oxide and calcium oxide fair mullite formers. They noted that the effect due to oxide concentration was small over a wide range and that the effectiveness of the oxides varied with temperature.

Budnikov and Shmakler⁹, also, using hydrofluoric acid and X-ray methods, found that the addition of mineralizers lowered the point at which mullite formation started by 100° to 200° C. The mineralizers they used in descending order of effectiveness were as follows:

(a) At 1400° C.

2% MnO, 1% MgCl₂, 2% TiO₂, 4% CaF₂

(b) At 1500° C.

2% MnO, 2% TiO₂, 4% Cr₂O₃, 4% MgCl₂,
4% Fe(OH)₃, 2% CaCl₂

(c) At 1600° C.

2% MnO, 2% TiO₂, 4% MgCl₂, 4% LiCl.

The investigators in the papers listed above have apparently either assumed or proven to their satisfaction that the addition of mineralizers increased the amount of mullite in the fired clay.

Navias¹⁰, using a special X-ray camera in which the diffraction patterns for reference standards were recorded with the pattern of the sample under investigation, concluded that the maximum quantity of mullite which could form was present after firing to cone 10.

Harvey and Birch¹¹, using a camera essentially the same as that used by Navias¹⁰, concluded that all of the mullite which could form was present after firing to Cone 11 and that firing to Cone 18 increased the size of the mullite crystals but not the amount.

III. EXPERIMENTAL PROCEDURE

The clay used was air floated Pioneer Georgia Kaolin of the following analysis:

SiO ₂	45.0%
Al ₂ O ₃	36.1
Fe ₂ O ₃	0.6
TiO ₂	1.6
Ignition loss	<u>14.7</u>
	99.0%

The catalytic agents used were all of c.p. quality except calcium fluoride which was a native powder. These materials were crushed through a 200 mesh sieve, weighed on a chainomatic balance to the nearest 0.0001 grams and intimately mixed with the kaolin by blunging in benzene. A benzene vehicle was used because suspensions of clay in benzene are thixotropic, this property prevents differential settling after blunging and during the drying period. Specimens measuring approximately 1/2" x 1/2" x 1-1/2" were dry pressed at 889 pounds per square inch on a Ben/ison Hydraulic Press, Model No. CP8003A12. These specimens were fired in a globar electric furnace, equipped with Wheelco controls, to 2600° F. with a half hour hold followed by an air quench.

To avoid contamination during firing the specimens were placed, with their 1-1/2" dimension vertical, in 1/2" x 1/2" x 1/2" deep holes in K30 insulating fire brick splits. Only the upper 1/4" of the fired specimens were used in the investigation.

After firing the specimens were crushed in a steel mortar through a 200 mesh sieve and carefully de-ironed with a hand magnet. Samples of the crushed material, weighing approximately 0.2000 grams, were

placed in platinum containers and digested for six hours in 10 ml of 40% hydrofluoric acid solution at 0° C. Three platinum crucibles and two platinum evaporating dishes were used in this investigation.

After acid treatment the specimens were washed, over filter paper, with 400 ml of distilled water. The weight of the residue, after ignition, was determined, to the nearest 0.0001 grams.

In preliminary work it was found that there was an effect due to containers, the platinum crucibles giving higher values than the evaporating dishes. Since the amount of stirring, during acid treatment, was also found to have an effect upon results a stirring procedure was developed to make the results from the different containers comparable. The specimens in the evaporating dishes were stirred with a platinum wire four times during the six hour acid treatment while those in the crucibles were stirred five times. There was a minimum of one hour between stirrings, the last stirring being made one hour before the six hour period ended.

All glassware was protected from the action of the hydrofluoric acid by a coating of paraffin.

The petrographic microscope was used to identify the principal crystalline phase in the fired specimens as mullite.

IV. EXPERIMENTAL DATA AND RESULTS

Catalytic materials were added to 100 gram batches of Pioneer Georgia Kaolin as indicated in Table I below:

Table I. CATALYTIC ADDITIVES

CATALYST	SYMBOL	CATALYST ADDED		% CATION	% ANION
		%	GRAMS		
CaCO ₃	CC1	0.250	0.250	0.100	0.150
	CC3	0.749	0.749	0.300	0.449
	CC5	1.249	1.249	0.500	0.949
K ₂ CO ₃	KC1	0.176	0.176	0.100	0.076
	KC3	0.530	0.530	0.300	0.230
	KC5	0.883	0.883	0.500	0.383
Na ₂ CO ₃	NC1	0.230	0.230	0.100	0.130
	NC3	0.692	0.692	0.300	0.392
	NC5	1.152	1.152	0.500	0.652
Li ₂ CO ₃	LC1	0.532	0.532	0.100	0.432
	LC3	1.597	1.597	0.300	1.297
	LC5	2.662	2.662	0.500	2.162
CaCl ₂	CCL1	0.277	0.277	0.100	0.177
	CCL3	0.831	0.831	0.300	0.531
	CCL5	1.386	1.386	0.500	0.886
KCl	KCL1	0.191	0.191	0.100	0.091
	KCL3	0.572	0.572	0.300	0.272
	KCL5	0.954	0.954	0.500	0.454
NaCl	NCL1	0.254	0.254	0.100	0.154
	NCL3	0.763	0.763	0.300	0.463
	NCL5	1.272	1.272	0.500	0.772
LiCl	LCL1	0.611	0.611	0.100	0.511
	LCL3	1.834	1.834	0.300	1.534
	LCL5	3.057	3.057	0.500	2.557
CaF ₂	CF1	0.195	0.195	0.100	0.095
	CF3	0.584	0.584	0.300	0.284
	CF5	0.974	0.974	0.500	0.474
NaF	NF1	0.183	0.183	0.100	0.083
	NF3	0.548	0.548	0.300	0.248
	NF5	0.913	0.913	0.500	0.413

TABLE I. CATALYTIC ADDITIVES, (cont.)

CATALYST	SYMBOL	CATALYST ADDED		% CATION	% ANION
		%	GRAMS		
LiF	LF1	0.374	0.374	0.100	0.274
	LF3	1.121	1.121	0.300	0.821
	LF5	1.869	1.869	0.500	1.369
KBr	KB1	0.304	0.304	0.100	0.204
	KB3	0.913	0.913	0.300	0.613
	KB5	1.522	1.522	0.500	1.022
NaBr	NB1	0.448	0.448	0.100	0.348
	NB3	1.343	1.343	0.300	1.043
	NB5	2.239	2.239	0.500	1.739

The sizes of the platinum containers used are indicated in Table II below:

TABLE II. PLATINUM CONTAINER SIZES

CONTAINER NUMBER	CONTAINER TYPE	DIAMETERS (mm)		HEIGHT (mm)
		TOP	BOTTOM	
E1	Evap. Dish	7.0	Round	3.5
E2	Evap. Dish	7.0	Round	3.5
C1	Crucible	4.1	2.2	3.5
C2	Crucible	4.1	2.2	3.5
C3	Crucible	2.8	1.7	3.2

A. PRELIMINARY INVESTIGATION

The samples in the evaporating dishes presented a greater surface to the action of the acid, in the quiescent period between stirrings, than they did in the crucibles. This was due to the fact that the particles had a larger area over which to settle in the evaporating dishes.

The results of the investigation into the effect of containers

on results and the investigation of the possibility that decreasing sample size and varying the stirring procedure would serve to correct any of these effects, are listed in Table III. All samples except NA13, NA14, NA17, and NA18 were stirred four times during the acid treatment with a minimum of one hour between stirrings, the last stirring being completed one hour before the six hour treatment period ended. In the case of the samples, to which exception was made above, the stirring procedure differed in that they were stirred five times during the acid treatment.

B. THE INVESTIGATION

TABLE III. EFFECT DUE TO CONTAINERS AND SAMPLE SIZE

SAMPLE NO.	CRUCIBLE NUMBER	WT. OF SAMPLE (GMS.)	RESIDUE*	
			GMS.	%
NA1*	E1	0.5011	0.1448	28.9
NA2	E2	0.5008	0.1431	28.6
NA3	C1	0.4994	0.1667	33.4
NA4	C2	0.5052	0.1652	32.7
NA5	C3	0.5029	0.1924	38.3
NA6	E1	0.2002	0.0493	24.6
NA7	E2	0.2006	0.0512	25.5
NA8	C1	0.2008	0.0556	27.7
NA9	C2	0.2031	0.0578	28.5
NA10	C3	0.2004	0.0582	29.0
NA11	E1	0.2018	0.0507	25.1
NA12	E2	0.2015	0.0498	24.7
NA13	C1	0.2003	0.0509	25.4
NA14	C2	0.2021	0.0503	24.9
NA15	E1	0.2039	0.0514	25.2
NA16	E2	0.2010	0.0502	24.9
NA17	C1	0.2015	0.0512	25.4
NA18	C2	0.2047	0.0514	25.1

*NA indicates that no catalytic agents were added to the specimen from which this sample was taken.
^a after acid treatment.

TABLE IV. EFFECT OF CATALYTIC ADDITIONS

SAMPLE NUMBER	CRUCIBLE NUMBER	WT. OF SAMPLE (GMS.)	RESIDUE	
			GMS.	%
CC1-1	E1	0.2000	0.0615	30.8
CC1-2	G1	0.2017	0.0622	30.8
CC3-1	E2	0.2005	0.0680	33.9
CC3-2	G2	0.2010	0.0695	34.6
CC5-1	E1	0.2031	0.0640	31.5
CC5-2	G1	0.2022	0.0649	32.1
KC1-1	E2	0.2022	0.0538	26.6
KC1-2	G2	0.2005	0.0541	27.0
KC3-1	E1	0.2016	0.0538	26.7
KC3-2	G1	0.2028	0.0517	25.5
KC5-1	E2	0.2010	0.0525	26.1
KC5-2	G2	0.2022	0.0501	24.8
NC1-1	E1	0.2019	0.0509	25.2
NC1-2	G1	0.2023	0.0512	25.3
NC3-1	E2	0.2014	0.0486	24.1
NC3-2	G2	0.2006	0.0440	21.9
NC5-1	E1	0.2001	0.0416	20.8
NC5-2	G1	0.2022	0.0476	23.5
NC5-3	G1	0.2010	0.0455	22.6
LC1-1	E2	0.2019	0.0496	24.6
LC1-2	G2	0.2001	0.0483	24.1
LC3-1	E2	0.2000	0.0532	26.6
LC3-2	G2	0.2005	0.0508	25.3
LC3-3	E2	0.2014	0.0528	26.2
LC5-1	E1	0.2001	0.0560	28.0
LC5-2	G1	0.2017	0.0581	28.8
CC11-1	E1	0.2012	0.0573	28.5
CC11-2	G1	0.2020	0.0611	30.2
CC11-3	G2	0.2023	0.0591	29.2

TABLE IV. EFFECT OF CATALYTIC ADDITIONS, (cont.)

SAMPLE NUMBER	CRUCIBLE NUMBER	WT. OF SAMPLE (GMS.)	RESIDUE	
			GMS.	%
CC13-1	E1	0.2006	0.0644	32.1
CC13-2	G1	0.2042	0.0652	31.9
CC15-1	E1	0.2013	0.0606	30.1
CC15-2	G1	0.2000	0.0626	31.3
CC11-1	E1	0.2004	0.0553	27.0
CC13-1	G1	0.2023	0.0489	24.2
CC15-1	E2	0.2013	0.0415	20.6
CC11-1	E2	0.2028	0.0482	23.8
CC13-1	G2	0.2002	0.0461	23.0
CC15-1	G1	0.2035	0.0465	22.8
CC11-1	E2	0.2004	0.0637	31.8
CC11-2	G2	0.1997	0.0618	31.0
CC13-1	E2	0.2008	0.0709	35.3
CC13-2	G2	0.2013	0.0709	35.2
CC15-1	E1	0.2015	0.0727	36.1
CC11-1	G2	0.2004	0.0570	28.4
CC13-1	G1	0.2040	0.0555	27.2
CC15-1	G2	0.2029	0.0506	24.9
CC11-1	E1	0.2017	0.0522	25.9
CC13-1	E2	0.2012	0.0519	25.8
CC15-1	E1	0.2015	0.0505	25.0
CC11-1	G1	0.2008	0.0620	30.9
CC13-1	G2	0.2008	0.0652	32.5
CC15-1	G2	0.2029	0.0609	30.0
CC11-1	G2	0.2005	0.0688	34.3
CC11-2	E1	0.2016	0.0679	33.7

TABLE IV. EFFECT OF CATALYTIC ADDITIONS, (cont.)

SAMPLE NUMBER	CROCKILE NUMBER	WT. OF SAMPLE (GMS.)	RESIDUE	
			GMS.	%
NF3-1	O1	0.2007	0.0530	26.4
NF5-1	O2	0.2005	0.0514	25.6
NF5-2	E2	0.2013	0.0533	26.5
LF1-1	E2	0.2009	0.0663	33.0
LF3-1	E1	0.2009	0.0542	27.0
LF3-2	E2	0.2005	0.0532	26.7
LF5-1	E2	0.2017	0.0532	26.4

TABLE V. AVERAGES OF THE PERCENT RESIDUE AFTER ACID TREATMENT

PERCENT CATION	ANION		CARBONATE	CHLORIDE	FLUORIDE	BROMIDE
	CATION					
0.1	Calcium		30.8	29.6	30.9*	
	Potassium		26.8	27.0*		28.4*
	Sodium		25.2	23.8*	34.0	25.9*
	Lithium		24.4	31.4	33.0*	
0.3	Calcium		34.2	32.0	32.5*	
	Potassium		26.1	24.2*		27.2*
	Sodium		23.0	23.0*	26.4*	25.8*
	Lithium		26.0	35.2	26.8	
0.5	Calcium		31.8	30.7	30.0*	
	Potassium		25.4	20.6*		24.9*
	Sodium		22.3	22.8*	26.0	25.0*
	Lithium		28.4	36.1*	26.4*	

* These values are the result of one determination.

V. DISCUSSION OF RESULTS

It became apparent at the outset of the acid treatments that the results of the investigation were dependent on a number of factors of which we had not previously been aware. In order to secure comparable data it was necessary to conduct a preliminary investigation into the effects of containers, stirring and sample size on results.

A. EFFECT DUE TO CONTAINERS AND SAMPLE SIZE

Five platinum containers of three different sizes were used in this portion of the work, their measurements are listed in Table II on Page 7. Approximately 0.5 grams of a specimen to which no catalytic additions had been made were placed in each crucible and treated with hydrofluoric acid, the samples in all crucibles were subjected to the same stirring procedure.

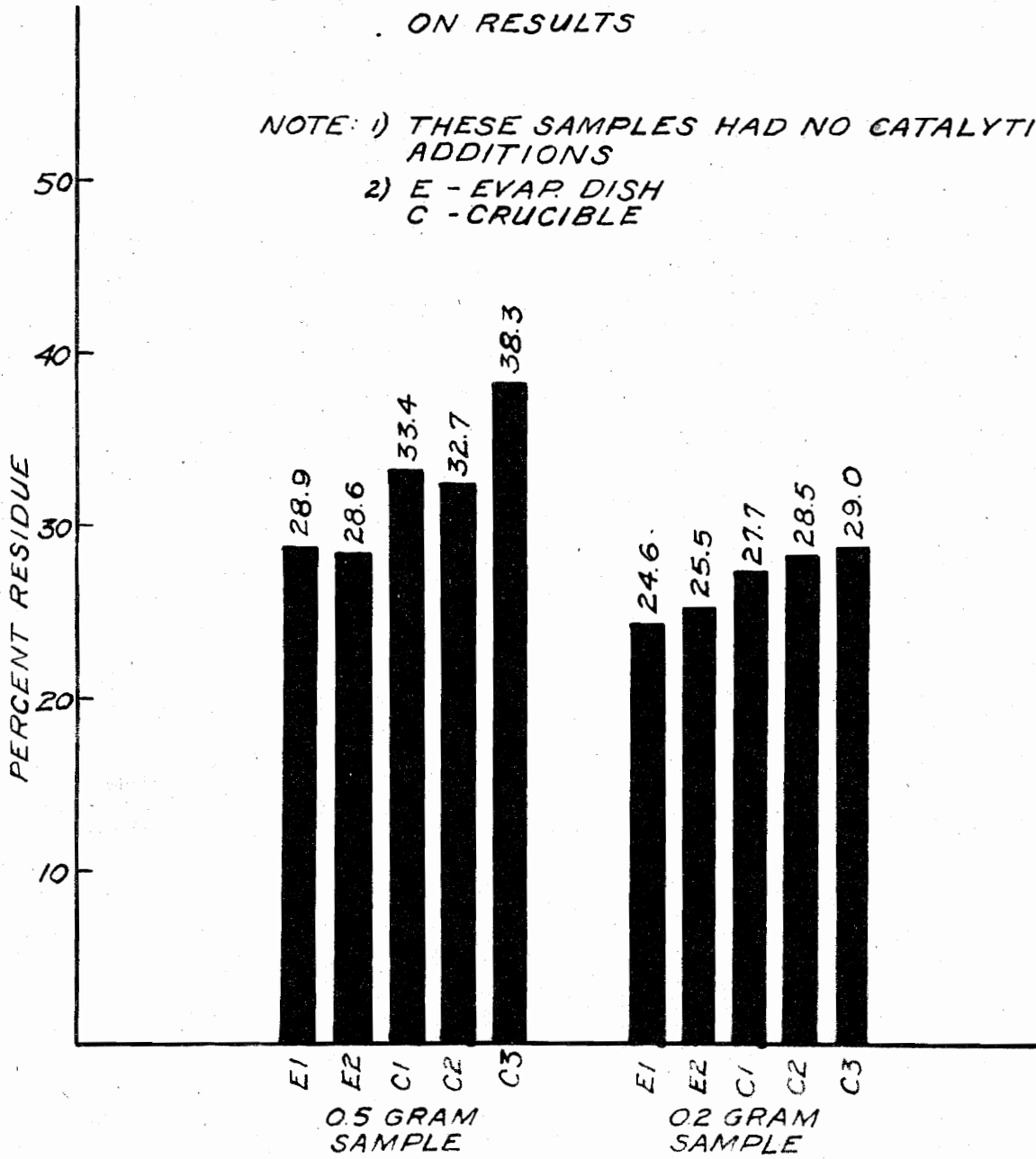
After acid treatment it was found that the large crucibles contained approximately five percent more residue than the evaporating dishes and the small crucibles approximately 10%. These results are shown in the left hand portion of graph No. 1, page 13. The 0.2 gram samples portrayed on the right of this graph show that decreasing the sample size does partially correct for the variation due to containers.

A possible explanation of this variation is the manner in which the particles of the sample settle in the different containers. In the crucibles the particles tend to settle, and pile up, over a relatively smaller area than in the evaporating dishes, thereby exposing less surface area to the action of the acid between stirrings. When sample size is decreased there is a smaller proportion of the sample hidden,

GRAPH NO. 1

EFFECT OF
CONTAINER AND SAMPLE SIZE
ON RESULTS

NOTE: 1) THESE SAMPLES HAD NO CATALYTIC
ADDITIONS
2) E - EVAP. DISH
C - CRUCIBLE



due to settling, from the action of the acid, thereby giving less apparent variation between containers. Consideration of this phenomena led us to choose a sample size of 0.2 grams for subsequent determinations.

B. EFFECT OF VARYING STIRRING SCHEDULE

It was felt that if a different stirring procedure was used for samples in the crucibles, than was used for those in the evaporating dishes, comparable results could be secured from the different containers. To establish this theory a series of determinations were made in which the samples in the crucibles were stirred five times, during the acid treatment, while those in the evaporating dishes were stirred four times as before. The results of these determinations, which consisted of two replications in the evaporating dishes and large crucibles, are shown in Graph No. 2, on page 15 - use of the small crucible was discontinued. It can be seen that the revised stirring schedule has, for our purpose, eliminated the effect due to containers. In view of these observations this stirring schedule, outlined in the experimental procedure, was used in subsequent determinations. An average of the values for percent residue, listed in the last half of Table III and shown in Graph No. 2, was established as an indication of the mullite development in kaolin samples containing no additives.

C. THE RELATIVE EFFECT OF VARIOUS COMPOUNDS ON MULLITE DEVELOPMENT IN KAOLIN

1. CALCIUM COMPOUNDS

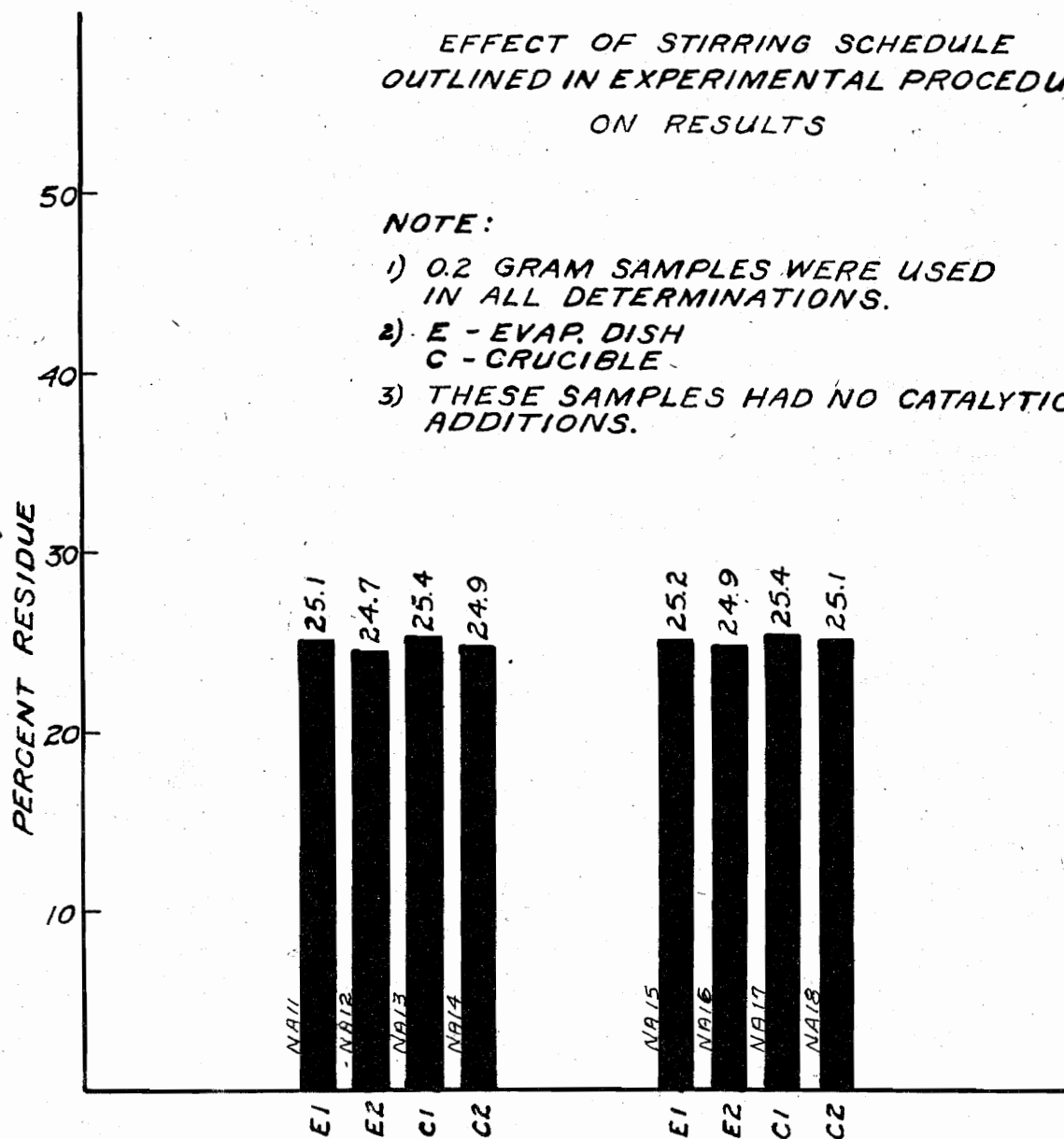
Considering Graph No. 3, page 16: The effectiveness of the various calcium compounds arranged in order of decreasing effectiveness

GRAPH NO. 2

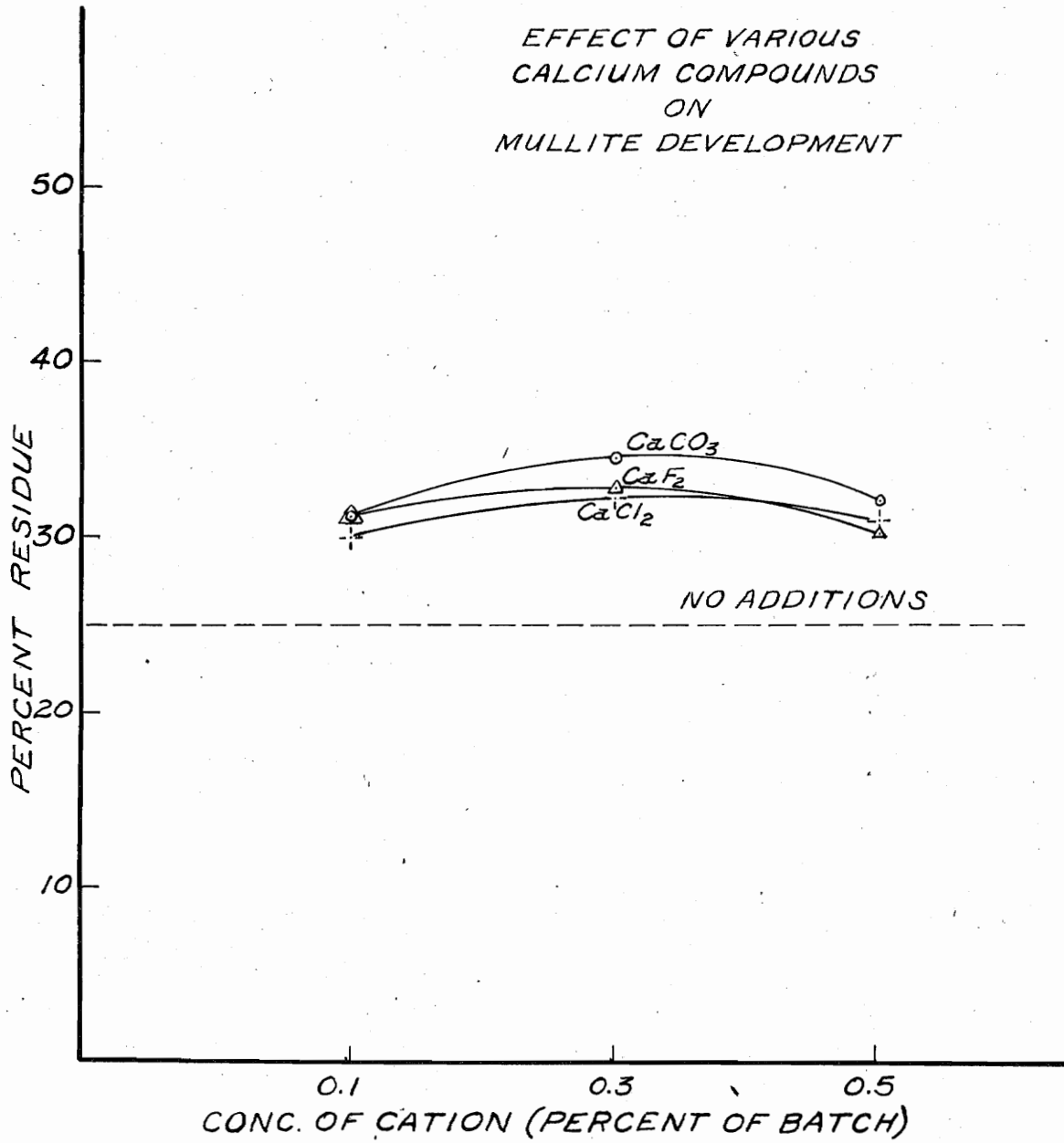
EFFECT OF STIRRING SCHEDULE
OUTLINED IN EXPERIMENTAL PROCEDURE
ON RESULTS

NOTE:

- 1) 0.2 GRAM SAMPLES WERE USED IN ALL DETERMINATIONS.
- 2) E - EVAP. DISH
C - CRUCIBLE
- 3) THESE SAMPLES HAD NO CATALYTIC ADDITIONS.



GRAPH NO. 3



are: in low and intermediate concentrations of calcium; (a) carbonate, (b) fluoride, (c) chloride, and in calcium concentrations greater than 0.4%; (a) carbonate, (b) chloride, (c) fluoride. It is apparent that the effectiveness of these compounds slowly increases with increasing calcium concentration up to about 0.3%, after which their effectiveness decreases. In general, it can be said that all of the calcium compounds investigated are very effective mineralizers over the concentration range studied.

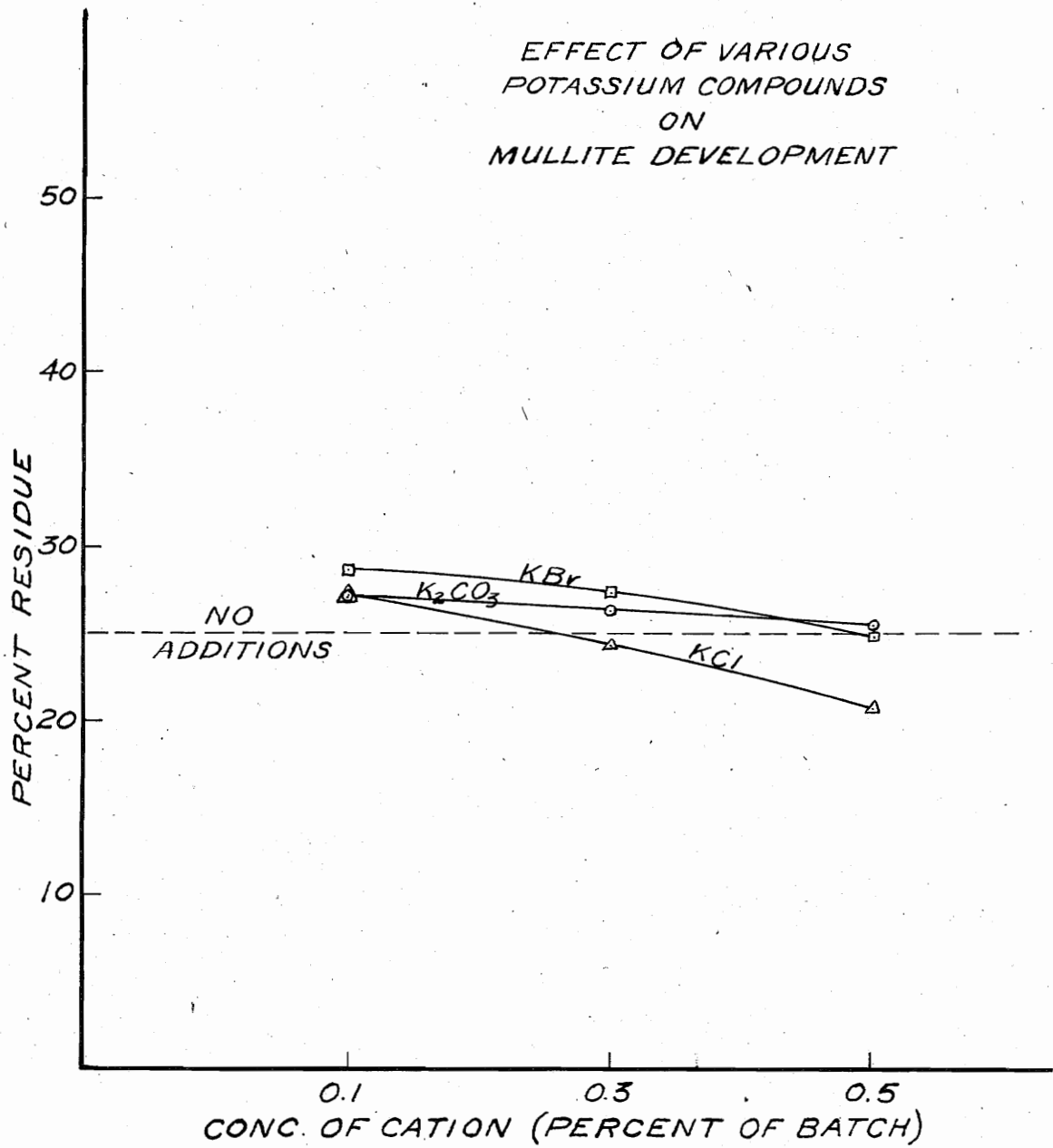
2. POTASSIUM COMPOUNDS

Considering Graph No. 4, page 18: The effectiveness of the various potassium compounds arranged in order of decreasing effectiveness are; in low and intermediate concentrations of potassium, (a) bromide, (b) carbonate, (c) chloride, and in concentrations greater than about 0.4% potassium, (a) carbonate, (b) bromide, (c) chloride. The effectiveness of all these compounds decreased with increasing concentration. The chloride loses its effectiveness at concentrations greater than 0.3% potassium and begins to suppress mullite development, this suppressive effect becomes very marked at a potassium concentration of 0.5%. The bromide and chloride begin to suppress mullite development in potassium concentrations greater than 0.5%.

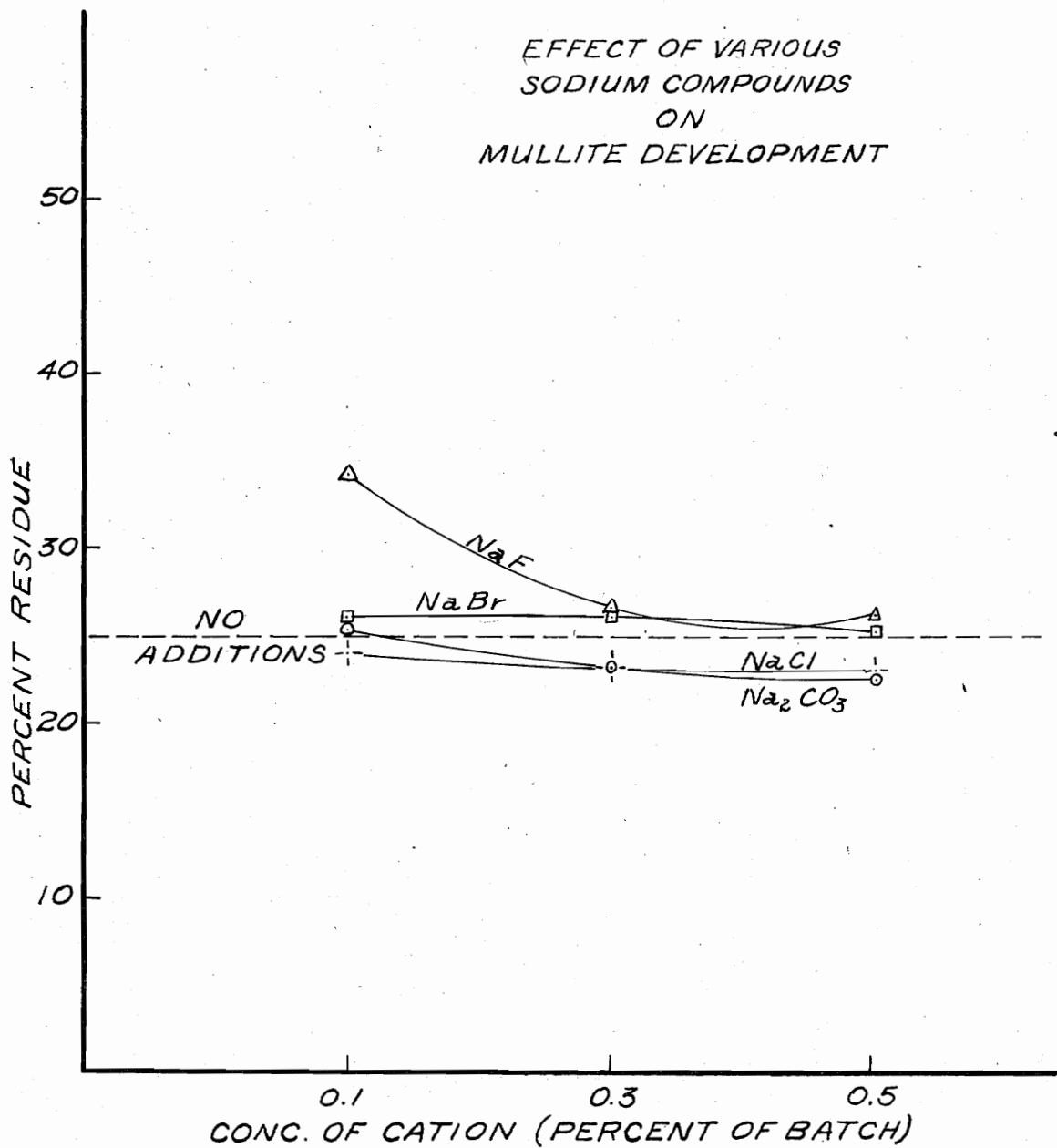
3. SODIUM COMPOUNDS

Considering Graph No. 5, page 19: The effectiveness of the various sodium compounds arranged in order of decreasing effectiveness are in all concentrations of sodium, (a) fluoride, (b) bromide, (c) carbonate-chloride. The carbonate and chloride tend to suppress mullite

GRAPH NO. 4



GRAPH NO. 5



development while the bromide has a slight catalytic effect which decreases only slightly with increasing concentration. The fluoride is a very good mineralizer in low concentrations showing a sharp decrease in effectiveness as concentration increases.

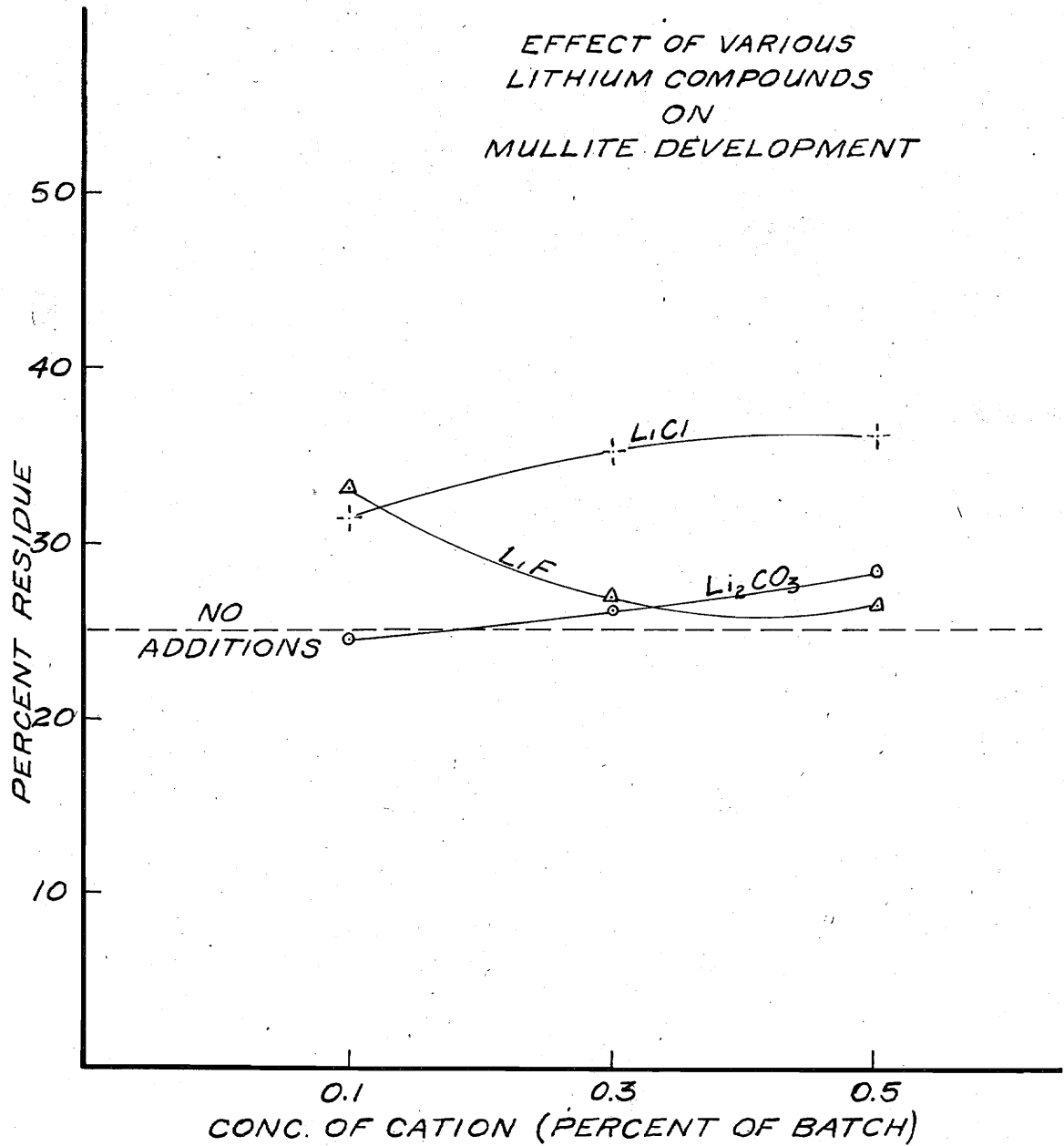
4. LITHIUM COMPOUNDS

Considering Graph No. 6, page 21: The effectiveness of the various lithium compounds arranged in order of decreasing effectiveness are: at low concentrations of lithium, (a) fluoride, (b) chloride, (c) carbonate; at intermediate concentrations, (a) chloride, (b) fluoride, (c) carbonate; and at high concentrations, (a) chloride, (b) carbonate, (c) fluoride. The chloride appears to be a very good mineralizer in all concentrations of lithium, the fluoride is very good at low concentrations but rapidly loses effectiveness as concentration increases, while the carbonate suppresses mullite development at low lithium concentrations and becomes a fair mineralizer at high concentrations. There is no general trend which can be attributed to the lithium cation.

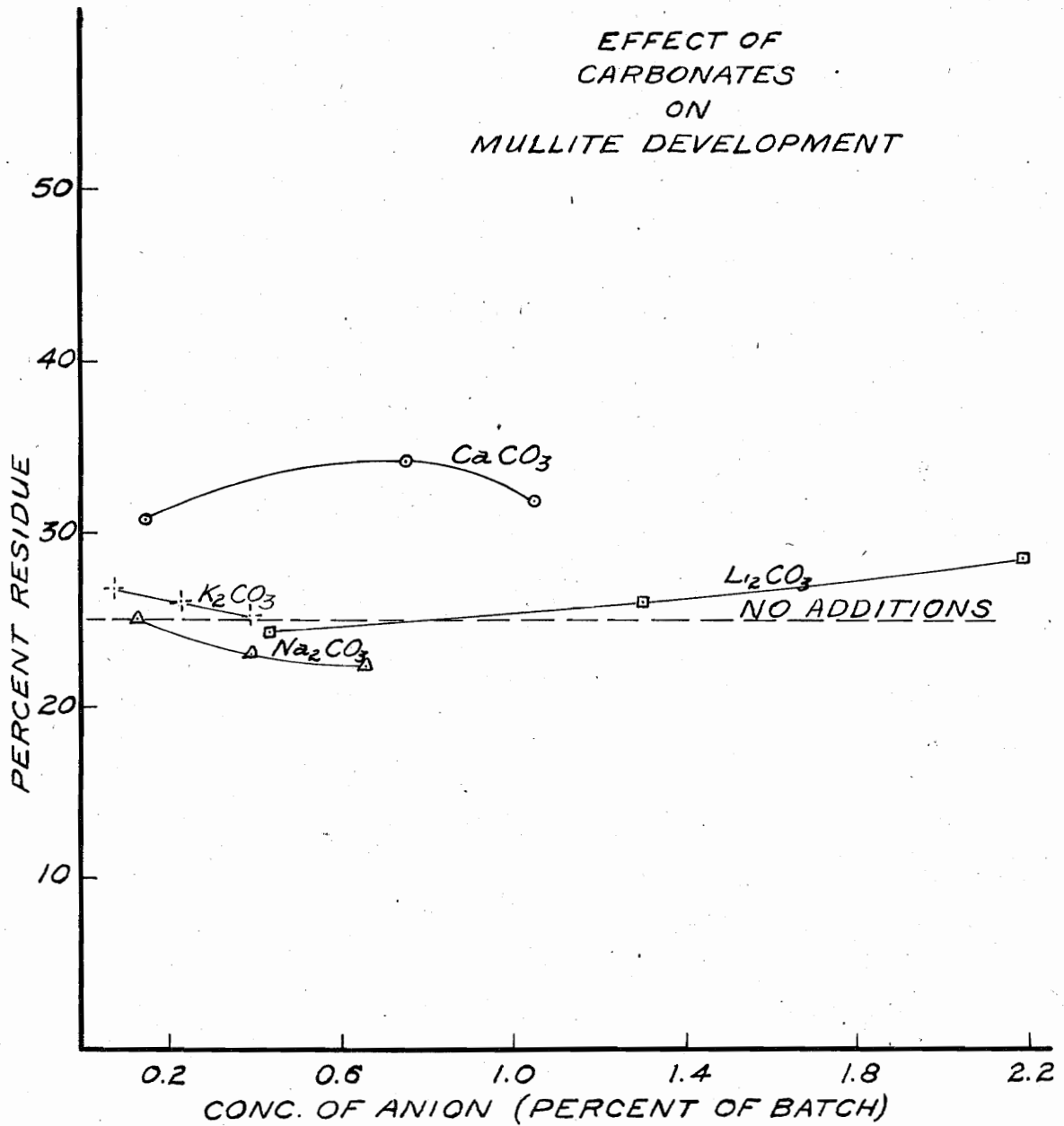
5. EFFECT OF THE ANION ON MULLITE DEVELOPMENT

As shown by Graph No. 7, the carbonate anion does not have a regular effect on mullite development over all the compounds and concentrations investigated, the same can be said of the chloride anion as shown by Graph No. 8. The fluoride shows a definite decrease in catalytic activity in the higher concentrations as portrayed in Graph No. 9, while the bromide (Graph No. 10) shows no specific trend

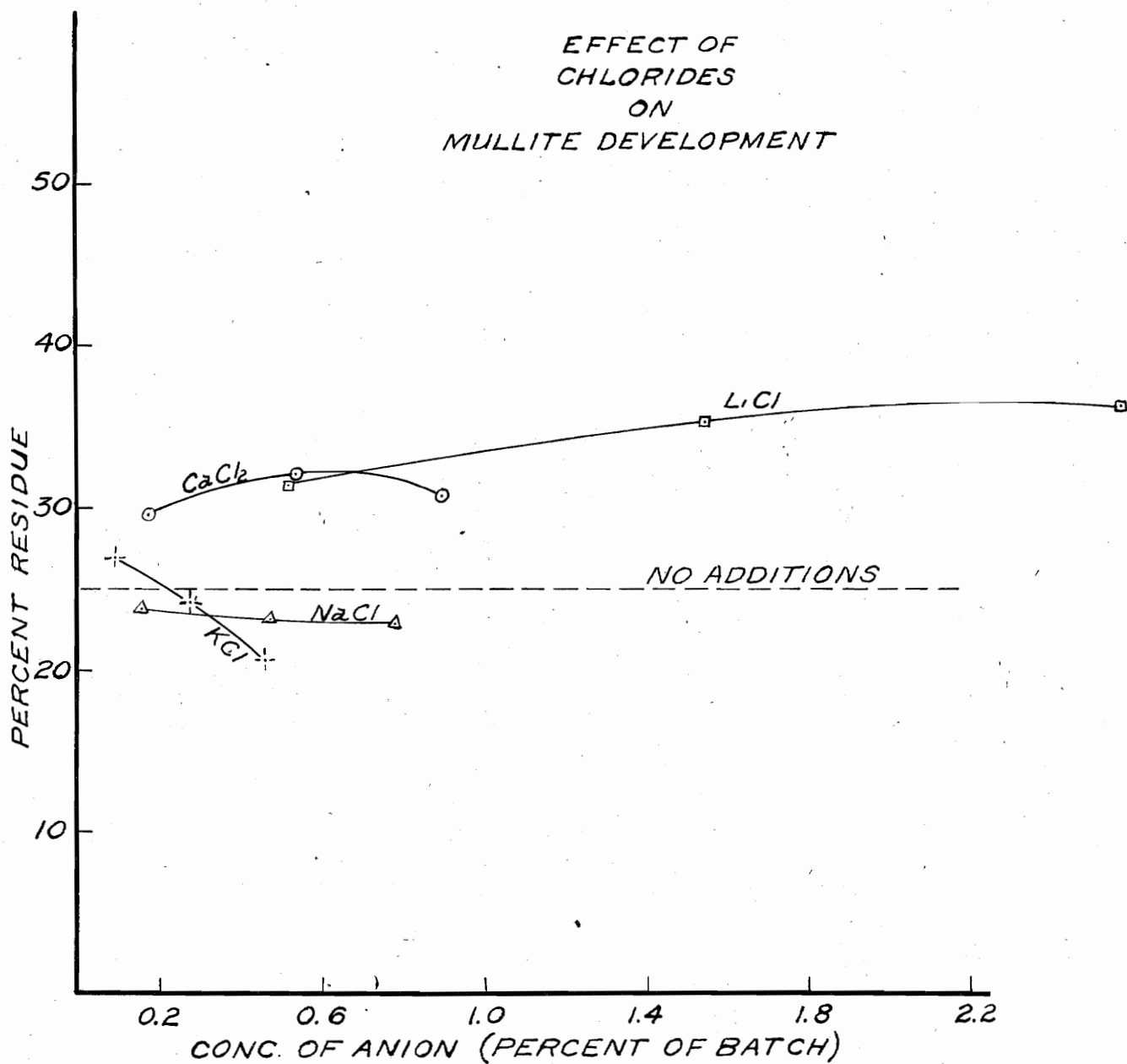
GRAPH NO. 6



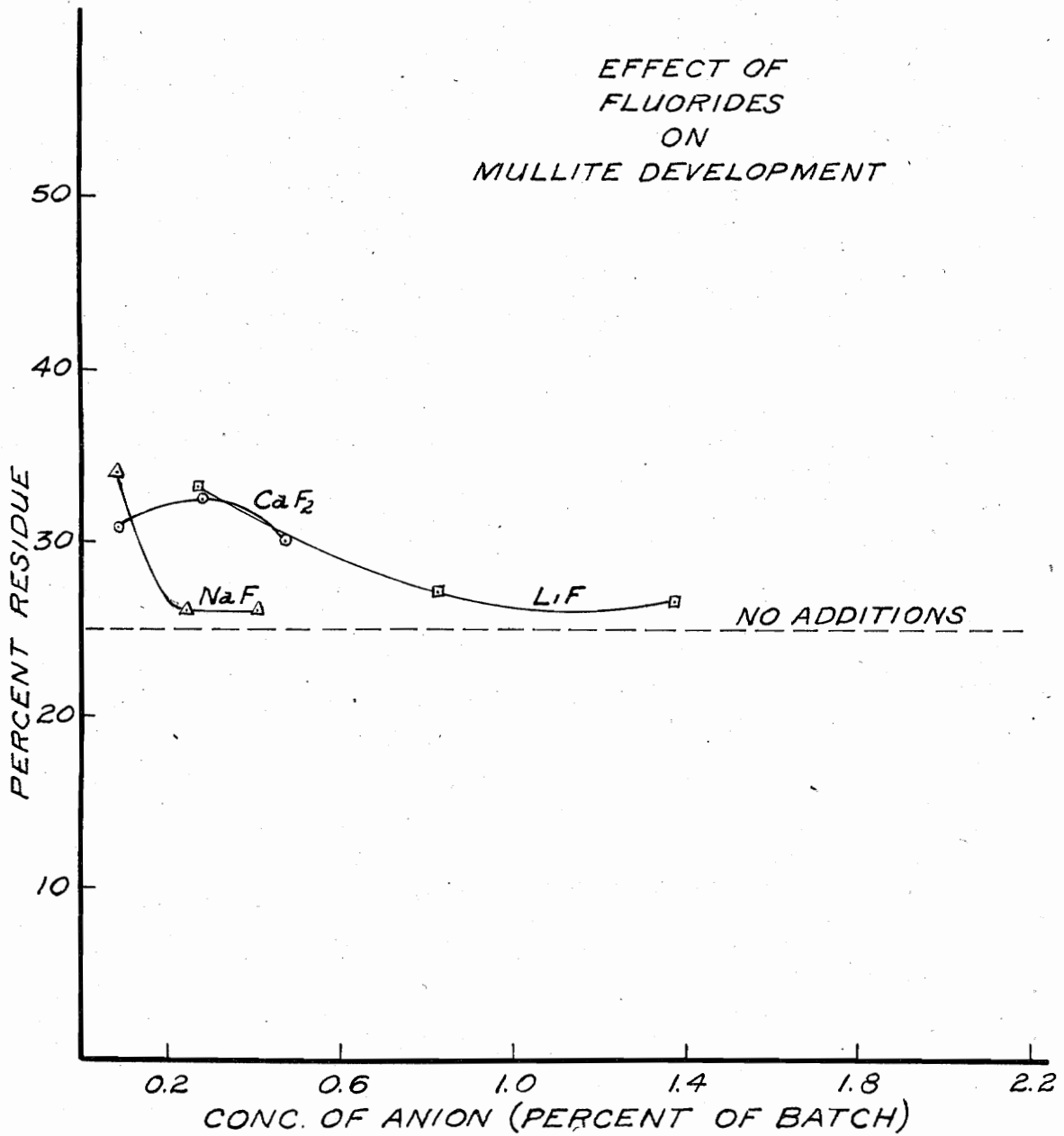
GRAPH NO. 7



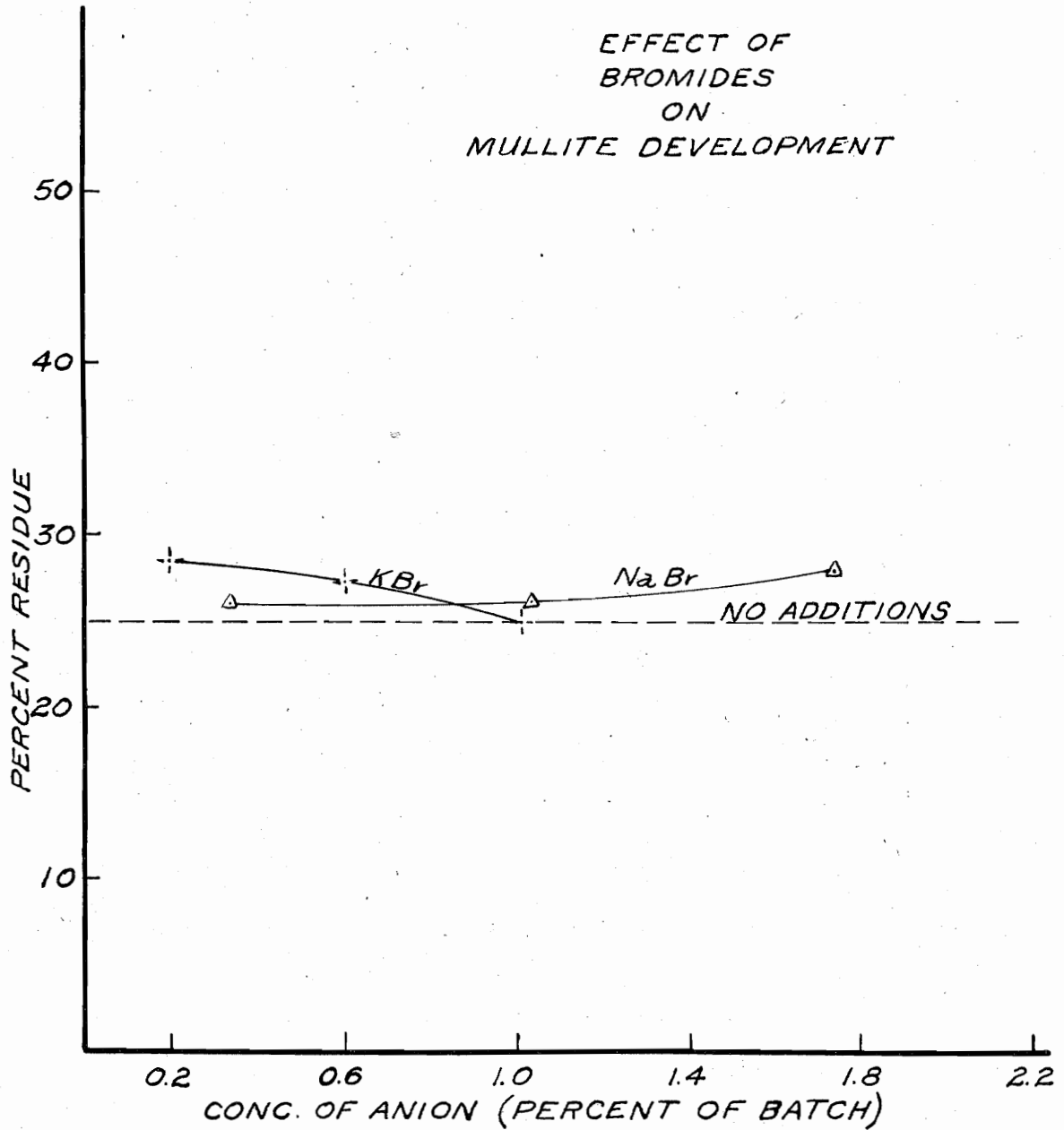
GRAPH NO. 8

EFFECT OF
CHLORIDES
ON
MULLITE DEVELOPMENT

GRAPH NO. 9

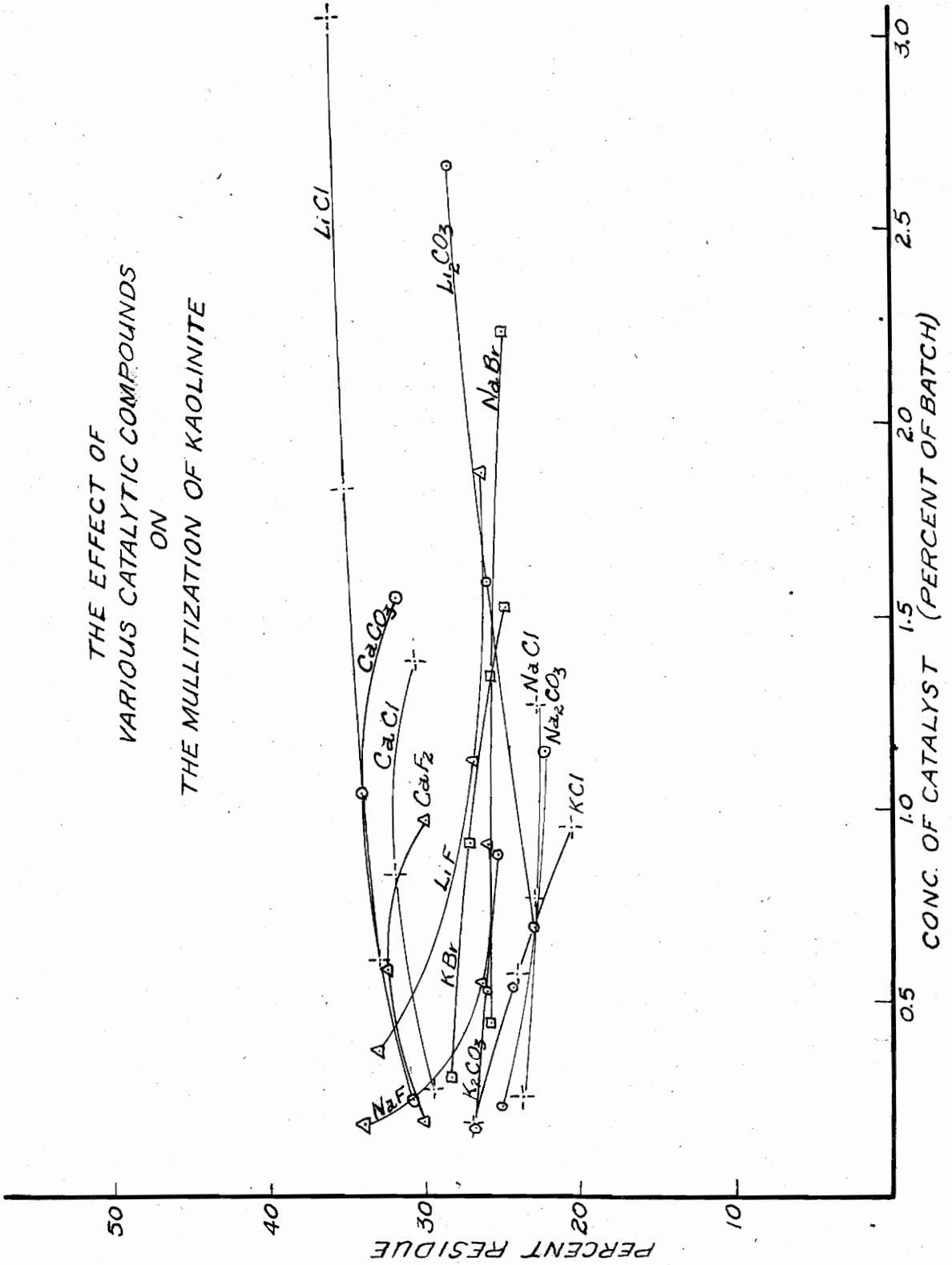


GRAPH NO. 10



GRAPH NO. 11

THE EFFECT OF
VARIOUS CATALYTIC COMPOUNDS
ON
THE MULLITIZATION OF KAOLINITE



but its effect could possibly be said to be relatively regular over the concentration range studied.

Graph No. 11, page 26, showing percent residue vs concentration of the catalytic compound h_2s has been included to give a picture of the relative activity of the catalytic materials used in this investigation.

VI. CONCLUSIONS

As a result of this investigation, we have found that the anion of the catalyst does enter into the catalytic reaction although its effect is not as pronounced as that of the cation.

Calcium seems to be the most stable cation investigated, apparently affected least by the anions in its compounds and all of its compounds were among the best mineralizers studied.

Lithium was affected most by the anions in its compounds. Considering the entire concentration range, lithium chloride was the best mineralizer studied while the carbonate could be rated as only fair and the fluoride as good only in low concentrations.

Sodium and potassium were slightly affected by the anions of their compounds except the fluoride of sodium which, at low concentrations, proved to be a very effective mineralizer, otherwise these compounds can be rated only as fair to poor mineralizers.

The fluoride is the only anion which exhibited a uniform effect, in all its compounds, over the concentration range investigated, its catalytic activity decreased as the concentration increased.

VII. BIBLIOGRAPHY

1. E. S. Shepard, G. A. Rankin and F. E. Wright; THE $Al_2O_3-SiO_2$ SYSTEM, Amer. Jour. Sci., 28(4)293-333(1909).
2. N. L. Bowen and J. W. Greig; THE SYSTEM $Al_2O_3-SiO_2$, Jour. Amer. Cer. Soc., 7(4)238-254(1924).
3. N. L. Bowen, J. W. Greig, and E. G. Zies; MULLITE - A SILICATE OF Al_2O_3 , Jour. Wash. Acad. Sci., 14, 183-191(1924).
4. P. B. Budnikov and B. A. Khish; MULLITIZATION OF REFRACTORY GGGG MATERIAL, Ber. deut. keram. Ges., 10(10)445-448(1929); Cer. Abs., 9(2)108(1930).
5. P. B. Budnikov, INCREASING CHEMICAL RESISTANCE OF REFRACTORIES FOR GLASS TANKS, Ber. deut. keram. Ges., 15(10)505-513(1934); Cer. Abs., 14(6)141-142(1935).
6. T. Y. Oshioka and M. Isomatsu; STUDY OF MULLITE, Jour. Japan. Cer. Assoc., 28, 200-208, 705-710(1930); Refractories Bibliography, 2021e, Am. Iron and Steel Inst. and Am. Cer. Soc., Columbus, Ohio (1950).
7. T. Nakai and Y. Fukami; MINERALIZERS EFFECTIVE FOR THE CRYSTALLIZATION OF MULLITE, Jour. Japan Cer. Assoc., 47(557)225-228(1939); Refractories Bibliography, 1272f, Am. Iron and Steel Inst. and Am. Cer. Soc., Columbus, Ohio(1950).
8. G. W. Parmelee and A. R. Rodrigues; CATALYTIC MULLITIZATION OF KAOLINITE BY METALLIC OXIDES, Jour. Amer. Cer. Soc., 25(1)1-10(1942).
9. P. B. Budnikov and K. M. Shaukler; EFFECT OF MINERALIZERS ON THE PROCESS OF MULLITIZATION OF CLAYS, KAOLINS, AND SYNTHETIC MASSES, Jour. Applied Chem. (U.S.S.R.), 19(10-11)(1029-1036(1946);

Refractories Bibliography, 2:51, Am. Iron and Steel Inst. and Am. Cer. Soc., Columbus, Ohio(1950).

10. L. Navias; QUANTITATIVE DETERMINATION OF THE DEVELOPMENT OF MULLITE IN FIRED CLAYS BY AN X-RAY METHOD, Jour. Amer. Cer. Soc., 8, 296-302(1925).

11. F. A. Harvey and R. E. Birch; MULLITE DEVELOPMENT IN SUPER DUTY FIRECLAY BRICK, Jour. Amer. Cer. Soc., 19(11)322-327(1936).