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BY

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INVESTIGATION OF METHODS FOR THE PRODUCTION OF METALLIC POTASSIUM

Report

to

the Director of

The Naval Research Laboratory

by

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INVESTIGATION OF METHODS FOR THE PRODUCTION OF METALLIC POTASSIUM

I. FOREWORD

The present investigation, which was initiated November 8, 1940, was undertaken for the purpose of examining and developing processes whereby metallic potassium or sodium-potassium alloys of high potassium content might be produced commercially. The results of earlier investigations have been fully detailed in two reports under date of June 6, 1941 and September 1, 1941, respectively. For the sake of convenience, the significant results of the earlier work are briefly summarized below as are also those of more recent investigations. Included in the present report are results on the burning of potassium by the spray gun method. This method of converting the metal to the oxide is deserving of further investigation but can best be carried out at the Naval Research Laboratory where the necessary metal and other facilities are available.

The laboratory phase of this investigation has now been concluded; the results of the investigation have been incorporated in the design for a new pilot unit which is being installed at the Naval Research Laboratory. This unit will have a capacity of from 30 to 50 pounds of metallic potassium per charge. A complete, small pilot unit, having a capacity of about five pounds of metal and incorporating all the latest elements of design, was constructed in the Brown shops and is now in operation at the Naval Research Laboratory. This unit will supply much valuable engineering information which will be useful in connection with the operation of the larger pilot unit.

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II. SUMMARIES

A. Report of June 6, 1941. The reaction between sodium and potassium fluoride in the liquid phase was investigated. The metal, as distilled from the reaction mass under atmospheric pressure, contained from 75.4 to 93.3 atom percent of potassium as the sodium added varied from 1.0 to 0.25 atoms per mole of salt. The salt was introduced into a large, stainless steel pot along with the desired amount of sodium; it was heated electrically and when the reaction was completed, the salt was drained from the pot and a new charge was introduced. This process, while practicable, is undesirable from the point of view of cost of materials, since the cost of potassium fluoride per pound of metallic potassium is in the neighborhood of twenty-six cents.

Pure potassium was obtained with yields ranging as high as 82% by reacting calcium carbide with potassium fluoride at temperatures in the neighborhood of 1000°C. There were some losses due to the reaction of nitrogen with carbon which takes place readily in the presence of metallic sodium or potassium. Under helium, the loss of metal due to such reaction may be eliminated. Under vacuum, the reaction can be carried out at temperatures between 800° and 900°C and yields have been obtained running as high as 87%. With sodium at fifteen cents per pound, there might be some saving in the use of calcium carbide as reducing agent. The difficulty of the process lies in that the residual products of reaction are solids and it is necessary to cool the reactor for purposes of emptying and recharging. Potassium carbide is formed as an intermediate

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product of the reaction, for which reason, it is necessary to operate under reduced pressure unless the temperature is raised toward 1000°C. At 800°, the metal comes over at a pressure of about 20 cm.

Calcium silicide reacts with potassium fluoride somewhat more readily than does calcium carbide. The yield at atmospheric pressure was 87% of exceptionally pure metal. The reaction is best carried out under vacuum between 800° and 900°C under which conditions, the yield is 90%, or better. The disadvantages of this process are the relatively high cost and the unavailability of calcium silicide and the necessity for cooling off the reactor for purposes of emptying and recharging.

B. Report of September 1, 1941. Potassium sulfide may be reacted with calcium carbide or calcium silicide with the production of metallic potassium. The reaction sets in above the melting point of potassium sulfide (850°C) and must be carried to 1000°C, or more, to bring it to completion. The yield in the case of either reducing agent does not exceed 50%.

Potassium sulfide has been reduced by means of iron, aluminum and magnesium. On reacting potassium sulfide with iron up to 1025°, the maximum yield obtained was 49%. On reacting potassium sulfide with aluminum at temperatures 800° - 900° and 950° - 1000°, the yields obtained were 54% and 50%, respectively. On reacting potassium sulfide with magnesium at temperatures between 775° and 1000°, a yield of 73% of potassium was obtained.

Potassium sulfide in the liquid phase may be advantageously reduced by means of metallic sodium; alloys of high potassium

content are obtained. The results follow:

Atoms Na per equivalent K_2S	1.0	0.8	0.5
Atom % K in alloy	61.6	72.6	85.2

Sodium reacts readily with potassium sulfide in the solid phase. In order to avoid melting of the salt, temperatures must be maintained below the boiling point of potassium and the metal must be distilled under reduced pressure. Typical results for a series of reactions carried out at 600° with varying amounts of sodium follow:

Na_2/K_2S	1.00	0.75	0.50	0.45	0.30
Atom % K in alloy	83.00	89.5	96.2	96.1	96.4

Potassium sulfide and sodium sulfide do not form mixed crystals; as reaction proceeds, an intermediate salt phase, NaSK, is formed and exists along with K_2S for additions of sodium below 0.5 atoms per equivalent of K_2S. Since we have, here, at a fixed temperature, two solid phases, a liquid and a vapor phase (four phases in all), the composition of all phases is fixed. The vapor in this system contains approximately 96 atom percent of potassium. For additions of sodium between 0.5 and 1.0 atoms of sodium per equivalent of salt, the K_2S phase has disappeared and a Na_2S phase has appeared. The vapor phase in this equilibrium contains approximately 70 atom percent of potassium. The metal, as actually obtained for additions between 1.0 and 0.5 atoms of sodium per equivalent of K_2S, is a mixture resulting from 1/2 mole of 96% alloy arising from the first reaction and an amount of 70% alloy, arising from the second reaction, corresponding to the excess of sodium above the ratio value 0.5.

Decreasing temperature of reaction leads to richer potassium alloys. For a Na_2/K_2S ratio of 0.75, the condensate

from the reaction had the following composition at a series of temperatures:

Temperature, °C:	500	550	600	700	750	800
Atom % K in alloy:	95.5	93.9	89.5	83.3	79.3	73.2

Preliminary studies were made of possible means of producing potassium sulfide by reduction of potassium sulfate. Reductions were carried out using carbon (in excess) as reducing agent. Complete reduction to K_2S could not be obtained, even on heating the reaction mass to well above 1000°C. Samples of the reduction product were treated with sodium and yielded alloys which were fairly rich in potassium but the total yield of potassium was only about 60% of the theoretical. The composition of the alloy ranged between 63 and 86 atom percent of potassium, depending upon the amount of sodium added. The chief difficulties of the potassium sulfide reaction are the ready oxidizability of potassium sulfide in air, its reactivity toward water vapor and the difficulty of reducing potassium sulfate to the sulfide.

Observations made in connection with the study of the reaction between sodium and solid potassium sulfide indicated that enrichment occurs when sodium vapor passes upward through a column of the solid salt. This enrichment process was investigated more particularly for the reaction between sodium and solid potassium fluoride. Carrying out the reactions at 600°C, and using one atomof sodium per mole of potassium fluoride, the alloy contained 77.8 atom percent of potassium. when the sodium was placed on top of the salt and then melted down. When the sodium was placed in a cup underneath the salt, the resulting alloy contained 87.7 atom percent of potassium.

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In another experiment, 0.9 atom of sodium was used per mole of KF; the sodium was introduced at the bottom of a chamber and above it was placed a column of KF 17" high. On distilling the metal at 600°, the condensate was found to contain 98.8 atom percent of potassium. Using the same ratio of sodium to salt, and distilling under atmospheric pressure, the alloy contains 78 atom percent of potassium.

Potassium carbonate was investigated as a possible salt for the production of potassium by reduction with sodium. Carrying out a series of reactions between 550° and 650° and using varying proportions of sodium to salt, the following results were obtained:

Temperature, °C	500	600	650
		% K in alloy	
Na_2/K_2CO_3 = 1.0	-	67.7	-
" = 0.75	92.2	85.6	69.7
" = 0.5	94.0	90.8	79.5

The sodium-potassium carbonate reaction is of great interest, since the alloys have a very favorable composition and the cost of the salt is relatively low.

C. Present Report. Using a 40" column of potassium carbonate at various temperatures below 700°C, the influence of various factors upon the composition of the resulting alloy was investigated. These factors included the ratio of sodium to total potassium carbonate in the column, the method of preparing the salt, the temperature and pressure of the sodium in the boiler, the mean density of the salt and the size of the salt particles.

The composition of the alloy depends greatly upon the ratio of sodium to total potassium carbonate. With this ratio varying

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from 0.5 to 0.9, the composition of the alloy varied from approximately 99 down to 90 atom percent of potassium. Other factors were of minor influence, but the temperature and pressure of the sodium in the boiler were found to be important since, at higher pressures, the rate of flow of vapor through the column may be greatly increased for a given drop in pressure in the column. While the size of the salt particles has but little influence on the composition of the alloy, the rate of flow of vapor through the column becomes quite low when the particles become smaller. Satisfactory results were obtained with salt particles ranging between 1/2" and 1/6". The mean density of the salt in the column has little influence on the composition of the alloy; it is, therefore, advantageous to operate with a salt of relatively high density since the denser the salt, the greater the amount of metal produced in a column of given dimensions.

Experiments were carried out with salt column 5.5' long and of 3" diameter. Owing to the throttling action of the openings between the boiler and the column proper, the rate of sodium flow could not be carried to as high a point as desirable, although, in the second column, a fairly satisfactory rate of flow was obtained. The results of these larger columns were much the same as with the previous small column; with the sodium to salt ratio of 0.5, the alloy contained 97 atom percent of potassium, while with a ratio of 1.0, the alloy contained 90 atom percent of potassium.

Experiments were carried out to determine whether or not the vapors of an alloy could be enriched by passing them through

a column of salt which was kept at a temperature such that the metal did not condense upon it. When the flow of vapor was a sufficiently slow one, very appreciable enrichment occurred. For example, operating under low pressure with the column at a temperature of 625° and the boiler at 500°C, and passing the vapors through the column at the rate of 4.7 g./min., an alloy, initially containing 85 atom percent of potassium was enriched to 97 atom percent of potassium. On the other hand, when the rate of flow of metal was increased to between 10 and 13 g./min., no substantial enrichment of the alloy was effected. It was found, however, that if the temperature of the column, particularly the top, was reduced to a point where metal condensed on the salt, very substantial enrichment occurred. With an alloy having an initial composition of 85 atom percent of potassium, the alloy obtained on passing through the column contained 98 atom percent of potassium.

These results led to a study of the mechanism of the enrichment process when sodium vapor passes upward through a column of salt. Using a 24" column and a Na_2/K_2CO_3 ratio of 0.5, the salt in the column on completion of the reaction was analyzed for potassium. Operating under conditions where sodium condensed on the salt, it was found that the enrichment occurred and was substantially completed in a relatively narrow zone of salt from 6" to 10" long.

Using a column 48" long and 1-1/2" in diameter, which was provided with a boiler at the bottom so arranged that condensed metal could flow back into the boiler, a series of experiments was carried out for the purpose of determining the

efficiency of the column as the salt in the column was kept at various temperatures. Operating with a boiler temperature of 610° with a column temperature of 615° at the bottom and 520° at the top and reacting 92% of the total potassium carbonate in the column, an alloy was obtained containing 98 atom percent of potassium. In general, the column operated less satisfactorily when the top of the column was kept at higher temperatures. These experiments showed conclusively that the column operates with a high degree of efficiency when the top of the column is kept at such a temperature that metal is condensed upon it and that only potassium is vaporized at the temperature existing at the top of the column. Reacting as much as 90% of the potassium carbonate in the column, alloys may be obtained containing 97 atom percent, or more, of potassium.

An investigation was carried out to determine the efficiency of a column packed with tubular metal rings. A 3" column was constructed with a reflux condenser at the top, a boiler at the bottom to which condensed metal was returned, and packed for 36" of its length with iron packing rings 3/8" long, 3/8" external diameter and 1/16" thickness. Approximately 900 cc. of an alloy containing 45 atom percent of sodium was distilled in the column under pressures of 15, 50 and 100 mm. The metal was collected in lots of approximately 100 cc. and a sample was taken at the beginning of the first 100 cc. and at the end of each succeeding 100 cc. of metal collected. The potassium content of these alloys was determined from cooling curves.

The column was found to be extraordinarily efficient.

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Practically 100% separation was obtained between the two metals. Thus, in one experiment, the sixth sample, taken off when 560 cc. of metal had been collected, melted at 63.1°C, corresponding to 99.8 atom percent of potassium. The seventh sample, taken off when 670 cc. of metal had been collected, melted at 89°C, corresponding to 2 atom percent of potassium. The metal remaining in the boiler was pure sodium.

The column was provided with thermocouple wells at intervals of 6" along the entire length of the packing and a movable exploratory thermocouple was provided whereby the temperature of the column could be obtained at any point. In the earlier stages of distillation, complete fractionation occurred in approximately 3" of packing and at the end, when practically all the potassium had been distilled off, complete separation was effected within 12" of packing. It is thus evident that a properly packed column provides an unusually simple and efficient means for the separation of potassium from sodium in their alloys. It is suggested that by providing a salt column with approximately 12" of packing at the top, pure potassium could be obtained in the distillate with a conversion of 90%, or more, of the potassium carbonate in the column.

It was thought that it might be possible to devise a process in which the salt in the form of solid particles could be passed continuously downward through a column, while sodium vapor was introduced at the bottom and the evolved potassium taken off at the top. Upon examination, it was found that such a process is not practicable because of the fact that

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potassium carbonate becomes tacky in the neighborhood of 400°C and will not flow properly above that temperature. Since the reaction must be carried out in the neighborhood of 550°C, or higher, a column cannot be made to function according to this principle. The tackiness of the salt may be reduced by admixing with it magnesium oxide. Using potassium carbonate containing as much as 50% of magnesium oxide, the tackiness is markedly reduced but yet does not flow satisfactorily at 550°C. Possibly, by increasing the magnesium oxide content of the salt, a column might be made to function but it is doubted that such a column would be practicable from an economic point of view.

The salt might be put into short containers, say 6" to 12" in length, which containers would be open at the top and provided with a screen at the bottom and these containers might be passed continuously through a column. Since the reaction must be carried out under vacuum, the mechanical difficulties of a process of this kind would seem to be such as to render it impractical.

Earlier experiments had shown that potassium sulfide may be reduced by means of sodium to produce an alloy of high potassium content. Experiments had also been carried out to produce potassium sulfide by reduction of potassium sulfate by means of carbon or reducing gases such as carbon monoxide. Further work was carried out on this problem but without satisfactory results. It was not found possible to completely reduce potassium sulfate to potassium sulfide at temperatures below 1000°. In view of the difficulty of producing potassium sulfide and its sensitivity to moisture and reactivity toward

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oxygen, it is concluded that the potassium sulfide process is not practicable at this time.

Incident to the production of metallic potassium, some experiments were carried out on the oxidation of potassium to K_2O_4 by atomizing the metal in a dry atmosphere by means of a spray gun. The method seems very attractive from the point of view of convenience and simplicity but it was not found possible to obtain the complete oxidation of potassium to K_2O_4; in other words, oxides lower than K_2O_4 were produced to a considerable extent.

It was found that the oxygen content of the resultant oxide was the higher, the higher the temperature at which the metal was burned. Such higher temperature was obtained by heating the air that operated the spray gun and by controlling temperature conditions in the burning chamber. It is conceivable that by increasing the oxygen content of the air, the temperature of the burning process might be brought to a point where oxidation to K_2O_4 would be complete. This, however, remains to be tested. That the metal was not completely oxidized to K_2O_4 was shown by treating the oxide with oxygen at temperatures between 100° and 200° C. When so treated, the oxide absorbed oxygen, in one case, for example, raising the oxygen content from 218 cc./g. to 227 cc./g.

III. PRELIMINARY STUDY OF THE K_2CO_3 COLUMN

Earlier investigations (summarized above) have led to two important results, namely: (1) when potassium carbonate in the solid state is reduced with sodium, the alloy obtained is rich in potassium; and (2) when sodium vapors are carried

upward through a column of a potassium salt in the solid state, a process of enrichment takes place as a result of which the alloy obtained is much richer in potassium than it is when distilled directly from the molten salt.

The reaction between sodium and solid potassium carbonate was studied in detail. For this purpose, the salt was introduced into a tube of 1-1/2" internal diameter to a height of approximately 40". At the bottom, the tube was provided with an enlarged chamber which served as boiler for the sodium. Various factors that might influence the composition of the alloy were investigated. These factors include: ratio of sodium to potassium carbonate in reactor, method of preparing the salt, temperature and pressure of the sodium in the boiling chamber, mean density of the salt and size of the salt particles.

A. Effect of Na_2/K_2CO_3 Ratio. A series of experiments was carried out at 625° (boiler temperature) in which the atomic ratio of metal to salt was varied between 0.5 and 0.9. In one series (Table I,A), the salt was of 4-10 mesh and in another (Table I,B) of 3/8"-6 mesh. The results are presented in Table I; the rate of distillation of sodium, in minutes required per 100 g. of sodium, is given in the last column.

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TABLE I

Effect of Na_2/K_2CO_3 Ratio on Alloy at 625°C

A. 4-10 mesh K_2CO_3

Exp. No.	Na_2/K_2CO_3	Atom % K in alloy	Minutes/100 g.Na
45	0.50	99.5	35
56	0.67	98.0	35

B. 3/8"-6 mesh K_2CO_3

60	0.50	96.8	33
61	0.67	94.4	42
62	0.90	89.5	30

As may be seen from the table, the alloy obtained is the richer in potassium, the lower the proportion of sodium added. The column is very effective; the alloys obtained in all cases are much richer than those obtained by other methods in which sodium is employed as reducing agent.

B. Effect of Method of Salt Preparation. Commercially, potassium carbonate is supplied in the form of a finely granular material. It cannot be used in this form in the column since the rate of flow of sodium vapor between fine particles at low pressures is extremely slow. It is, therefore, necessary to aggregate the material and thereafter to crush and classify it. There are two methods of aggregation: (1) to spray a layer of the material about 1/2" deep with water or a solution of potassium carbonate and thereafter dry it; or (2) to compress it into pellets or lumps of suitable size in a press. In the present study, the first method was used in most of the experiments. Initial drying of the hydrated material, which is preferably in the form of slabs about 1/2" thick, must be carried out below 135°C, since the

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hydrate melts at that temperature. The salt may be completely dehydrated by drying for 48 hours at 130° in a Grinnell dryer or it may be dried in a Grinnell dryer for a shorter period of time and thereafter in a vacuum dryer at a higher temperature. When dry, the salt is crushed and classified. Depending upon the method used to aggregate the salt, its mean density, as packed in a column, varies between the limits of 0.5 and 0.9.

The results for a series of experiments in which the salt was aggregated by a variety of methods are given in Table II. For the most part, the values given for the density of the salt and for the potassium content of the alloy, are averages for a considerable number of experiments.

TABLE II

Effect of Method of K_2CO_3 Preparation on Alloy

Na_2/K_2CO_3 = 0.5; t = 625°C; back p. = 15 mm.; 4-10 salt mesh

Exp. Nos.	Method of Preparation of Salts	Av.at.% K in alloy	Av.time min.per 100 g.Na	Av.Density K_2CO_3
67-81	Sheeting paste	96.5	33	0.77
82-85	Sheeting with sat.sol.	97.3	35	0.72
44-55	Spraying fines	95.4	34	0.70
25-39	Spray original salt w.H_2O	98.5	34	0.57
40-41	" " " w.sat.sol.	99.0	40	0.58
95	Pressed pills	98.6	49	0.73

As may be seen from the table, the potassium content of the alloy is not greatly dependent upon the method employed in preparing the salt. The alloys from experiments 44-55, from fines recovered from grinding salt samples, are consistently somewhat low in potassium and this may be significant. The same may be true of experiments 25-39 and 40-41, in which the original salt was aggregated by spraying with water and with saturated potassium carbonate solution; both preparations were

highly porous. Of special interest is the result of experiment 95 in which the original salt, which was anhydrous, was pressed into pellets. This method of preparing the salt for use in the column should prove highly advantageous in practice, since it avoids the sheeting and drying processes, both of which require considerable labor and equipment.

C. Effect of Boiler Temperature and Pressure. The manner in which the composition of the alloy is influenced by the pressure (which depends on boiler temperature) at which sodium vapor is introduced into the column is of much practical importance. The rate of flow of vapor through the column is limited by the pressure of the vapor. When a salt of small mesh or a long column of a coarser salt is used, the rate of flow of vapor through the column is limited by the density of the vapor.

The results of a series of experiments are given in Table III. The salt samples used in different experiments had the same mesh but were not identical preparations; they differed chiefly in density. In the table, ΔP is the pressure drop of the vapor in passing through the column and the back pressure recorded in the table is the pressure in the receiver. The pressure drop was nearly the same in all experiments.

[redacted]

TABLE III

Effect of Boiler Temperature and Pressure

Na_2/K_2CO_3 = 0.5; salt mesh = 4-6

Exp. Nos.	Boiler temp.	Back p.mm.	ΔP mm.	At. % K in alloy	Av. time per 100 g. Na
1-2	600	2	21	97.8	60
5-15	625	15	20	96.5	35
17-18	640	25	19	96.6	25
19	645	30	17	96.8	20

As may be seen on inspection of Table III, the composition of the alloy is not greatly dependent on the pressure of sodium vapor in the column. Allowing for the much lower rate of flow through the column at low pressures, it may be concluded that, other things being equal, the alloy produced at higher temperatures (and pressures) is, if anything, slightly richer in potassium than is that produced at lower temperatures. Of considerable practical importance is the observation that the alloy produced at 645° is nearly as rich in potassium as is that produced at 600°, while the rate of vapor flow at the higher temperature is three times that at the lower.

D. Effect of Mean Salt Density. Experiments were carried out to determine what influence, if any, the mean salt density might have on the composition of the alloy. In Table IV are given the results of a series of experiments.

[redacted]

TABLE IV

Effect of Mean Salt Density on Alloy

Na_2/K_2CO_3 = 0.5; t = 625°, back p. = 15 mm.; salt mesh = 4-10.

Exp. No.	Mean Salt Density	Minutes per 100 g.Na	At. % K in alloy
25	0.45	37	99.2
30	0.45	40	98.9
27	0.59	28	99.1
33	0.57	25	98.5
37	0.66	27	98.0
38	0.67	29	97.9
36	0.72	43	98.3
39	0.78	32	96.3

There appears to be a slight downward trend in the potassium content of the alloys as the density of the salt increases. The effect is not marked and the observed variations may be due to accidental factors. That such factors exist is made clear by the fact that, occasionally, wide variations in the potassium content of the alloy are obtained under what would seem to be identical conditions of operation. The nature of the factors that give rise to such variations will become clear from results to be presented in a later section (V) of this report.

E. Effect of Particle Size. It might be expected that the particle size of the salt in the column would have a marked influence on the efficiency of the column as a fractionating device. Experiments were carried out to determine whether or not such is actually the case. The results are given in Table V, A and B.

[redacted]

TABLE V

Effect of Particle Size on Alloy

Na_2/K_2CO_3 = 0.5; back p. = 15 mm.

A. t = 625°

Exp. Nos.	K_2CO_3 Mesh	At. % K in alloy	Min. per 100 g. Na	Av. Salt Density
44-55	4-10	98.4	34	0.70
57-59	3/8"-6	95.1	20	0.68

B. t = 605-615°

60	3/8"-6	96.8	33	0.73
63	1/2"-6	98.9	34	0.71
64	1/2"-6	96.6	31	0.65

The size of the salt particles has little or no effect on the composition of the alloy. Experiments 45-55 yielded a richer alloy than did experiments 57-59, but it is to be noted that in the latter reactions, the rate of flow of sodium vapor was much higher than in the former. In the experiments tabulated in Table V,B, the temperature (and pressure) was so regulated as to maintain the same rate of vapor flow through the column. Here, experiment 63, with the larger particles, yielded a richer alloy than did experiment 60 with smaller particles. On the other hand, in experiment 64, a duplicate of 63, the alloy had practically the same composition as that of experiment 60. It may be concluded that, except as it influences the rate of flow of metal vapor, the size of the salt particles in the column has little influence on the composition of the alloy. This is an important result since, if the rate of the reaction is to be stepped up, it is necessary to employ the salt in the form of large particles in order that a high rate of vapor flow may be obtained.

IV. STUDY OF THE K_2CO_3 REACTION IN LARGER COLUMNS

A. Action of 5.5' Columns. A number of reactions were carried out employing salt columns 5.5' long. The columns had a diameter of 3" and were provided with an external boiler at the bottom. From the boiler, the vapors passed through tubes into an anular chamber surrounding the bottom of the salt column. From the chamber, the vapor passed through holes or slots into the salt column proper. The columns were provided with a special closure at the bottom through which the converted salt could be emptied when the reaction was completed. The method of introducing vapor into the column did not prove entirely satisfactory, since the resistance to the flow of vapor through small holes or slots limited the rate at which sodium vapor could be passed through the column under given conditions of temperature and pressure of the boiler. The slotted arrangement was the more satisfactory of the two and permitted of a fair rate of vapor flow.

With the first column, in which the vapor was introduced through small holes, the reaction was studied largely from the point of view of the temperature and pressure of the boiler and the size of the salt particles. The results are given in Table VI.

[redacted]

TABLE VI

Results with First 5.5' Column

Exp. No.	Salt Mesh	Lbs. K_2CO_3	% Salt Reacted	Lbs. Alloy	At. % K in Alloy	Boiler Temp.	Rate g. Na per min.
1	4-10	13.4	61.7	4.25	97.2	635	8.0
2	4-10	12.9	71.5	3.94	97.3	652	8.5
3	4-8	12.4	67.2	4.68	96.5	643	6.6
5	4-8	12.7	67.2	4.75	95.5	637	7.3
6	4-6	12.2	65.0	4.62	98.0	642	8.2
7	4-6	9.7	67.5	3.81	97.3	648	8.1
8	4-6	9.4	67	3.56	96.9	640	9.0
9	4-6	10.6	67	4.06	96.7	649	8.5
10	4-6	10.4	66.8	3.94	96.8	637	8.0
11	3/8-6	8.8	68	3.38	95.6	641	8.0
12	3/8-6	10.9	67.8	4.19	95.9	623	6.2
13	3/8-6	11.7	50.5	3.38	97.9	637	8.2
14	3/8-6	11.6	88.7	5.56	94.8	630	9.5
15	3/8-6	11.6	67	4.19	96.0	642	10.2
16	3/8-6	11.7	64	4.13	96.6	642	9.6
17	1/2-6	11.7	67.2	4.38	95.4	646	8.4
18	1/2-6	9.7	74.6	1.56	97.1	645	7.5
19	1/2-6	11.6	67.3	3.88	96.0	642	10.9
20	1/2-6	11.1	67.0	3.88	96.3	648	10.2

The results, on the whole, were quite encouraging. With an equivalent Na_2/K_2CO_3 ratio of 0.89 (% salt reacted, col. 4), the alloy had a composition of 94.8 atom percent of potassium while, with a ratio of 0.67, the composition of the alloy ranged from 96.0 to 98.0 atom percent of potassium. The results indicate that, with a column of this type, as much as 90% of the potassium can be recovered from potassium carbonate in the form of an alloy containing above 90 atom percent of potassium. The results were not greatly influenced by the particle size of the salt used in the column. The rate of vapor flow could not be stepped up to the desired value because of the throttling action of the openings between the boiler and the reactor.

As stated, a second column was constructed in which the vapor from the boiler was carried into the reaction chamber through slots about 1/16" wide. The throttling action of

these slots was markedly smaller than that of the openings in the first column but they still exerted a marked influence upon the flow of vapor.

A series of reactions was carried out in which the equivalent ratio of sodium to salt was varied between 0.5 and 1.0. The results are presented in Table VII.

TABLE VII

Results with Second 5.5' Column. (1/2"-6 mesh)

Exp. No.	Lbs. K_2CO_3	% Salt Reacted	Lbs. Alloy	At. % K in Alloy	Boiler Temp.	Back Pres.	Rate g. Na per min.
1	12.3	67	4.50	96.0	640	15	6-17
2	12.4	67	4.38	95.0	640	15	17.1
3	12.4	80	5.44	93.0	640	15	16.0
4	11.8	50	3.10	97.1	637	15	14.8
5	11.8	100	6.25	90.0	650	15	20.2
6	11.3	67	3.69	96.0	635	10	18.0
7	11.3	67	3.81	95.7	632	10	19.0

In these experiments, the rate of flow of vapor through the column was approximately double that with the first column. The results were substantially the same as those with the first column although, perhaps, the alloys were slightly less rich than in the case of the first column. For an equivalent ratio of 0.67, the values average slightly under 96 atom percent of potassium as against values slightly above 96% in the case of column 1. With an equivalent sodium salt ratio of 0.5, the alloy contained 97.1 atom percent of potassium. With an equivalent sodium salt ratio of 1.0, the alloy contained 90 atom percent of potassium. Taken altogether, it may be concluded that a column of this type should serve to furnish potassium alloys containing from 90 to 95 atom percent of potassium on an economic basis.

[redacted]

B. Experiments on Enrichment of the Alloy by Means of 5.5' Column. It was thought that if alloys containing 90, or more, atom percent of potassium were vaporized and passed through a salt column, they might be enriched to such an extent as to serve as a means for producing practically pure potassium. A series of reactions was carried out using the second column, in which sodium-potassium alloys containing approximately 85 atom percent of potassium were vaporized in the boiler and passed through the column. The results are given in Table VIII.

TABLE VIII

Experiments on Enrichment of Alloy in 5.5' Column

Exp. No.	Lbs. of Na or Alloy	Salt Mesh	Salt Type	Column Temp.	Boiler Temp.	Rate g./min.	At. % K in Alloy
1	4.23 alloy	1/2-6	fresh	625	500	4.7	96.9
2	4.23 "	"	as in 1	625	545	11.7	<88
3	4.23 "	4-6	fresh	625	550	10.7	97.2
4	4.23 "	"	as in 3	575	545	11.7	<88
5	4.23 "	"	"	625	550	11.7	<88
6	1.67 Na	"	"	650	645	12.7	<88
7	1.71 Na	1/2-6	Fresh	650	630	11.9	97.2 Av. of 7 & 8
8	1.50 Na	"	as in 7	650	625	16.9	90.3
9a	1.41 alloy	"	Fresh	625	550	15.9	<88
9b	1.81 "	"	as in a	625	645	12.4	<88
9c	1.41 "	"	as in b	625	540	12.5	<88
10	1.89 Na	"	fresh	T550	645	-	97.2
11	2.03 Na	"	"	T575	630	13.0	96.6
12	1.3 Na	"	"	650	615	15.0	<88
13	2.82 alloy	"	"	T550	545	21	98
14	2.82 "	"	as in 13	T550	525	10	96.8
15	2.82 "	"	fresh	T550	525	7.1	98

As an examination of the table will show, the results of these experiments indicate clearly that the expected enrichment of the alloy did not occur. In experiment 1, in which the rate of flow of vapor was less than 5 g./min., the condensed alloy contained only 96.9 atom percent of potassium. This was a less rich alloy than that obtained, for example, in experiment 7, in which pure sodium was used. It is true that some enrichment

did occur, but the enrichment was far below that which might have been expected from the results obtained when pure sodium vapor is passed into the column. In experiments 2, 4, 5, 6, 9 and 12, the alloy contained less than 88 atom percent of potassium. In some cases, it was observed that the fresh salt operated more efficiently than did salt over which vapor from a preceding lot of alloy had been passed. For example, in experiment 3, the recovered alloy had a composition of 97.2 atom percent of potassium while, in experiments 4, 5 and 6, using the identical salt as in 3, the alloy contained less than 88 atom percent of potassium. Somewhat the same result was obtained in experiments 7 and 8, in which pure sodium was used.

On examining the results of the table carefully, it will be found that the governing factor that determined the composition of the resultant alloy was the temperature at the top of the column. In columns 5 and 6, are given, respectively, the temperature of the column and the temperature of the vapor in the boiler before entering the column. Up to experiment 10, the salt column was maintained at a uniform temperature along its length which temperature ranged from 575° to 650°. In experiments 10, 11, 13, 14 and 15, the temperature at the top of the column was reduced to 550° or 575°. The letter T before the temperature value in column 5, indicates that this represents the temperature at the top of the column. The temperature at the bottom of the column was maintained at 650° in all cases with the exception of experiment 15 in which it was 575°. The temperature of the boiler ranged, for the most part, from 545° to 645°. Except that the rate of vapor flow

through the column was greater at higher temperatures, the boiler temperature had little influence on the result.

It will be noted that in experiments 10 and 11, using pure sodium and maintaining the top of the column at 550° and 575°, the alloy obtained had a composition of 97.2 and 96.6 atom percent of potassium, respectively, while in experiment 12, where the entire column was maintained at a temperature of 650°, the alloy collected contained less than 88 atom percent of potassium. In experiments 14 and 15, where the boiler temperature was dropped to 525°, the alloys collected contained 96.8 and 98 atom percent of potassium, respectively. In experiment 13, with the top of the column at 550° and the boiler at 545°, and passing alloy through the column at the rate of 21 g./min., the alloy collected contained 98 atom percent of potassium.

The results obtained in the experiments described in this Section clearly indicate that the temperature at the top of the column has a critical influence upon the composition of the alloy which is collected. This observation led to a more detailed examination of the mechanism involved in the enrichment process of the salt column. The results of this study are given in the following Section.

V. MECHANISM OF THE ENRICHMENT PROCESS IN THE SALT COLUMN AND RESULTS WITH AN IMPROVED COLUMN

A. Mechanism. In the light of the results of the preceding Section, it seems clear that the enrichment of a sodium-potassium vapor in passing through a salt column is not primarily due to direct interaction between the vapor and the salt phase. What seems more likely is that when the hot vapor strikes the salt (at a lower temperature), it condenses

on the salt and a reaction takes place between liquid alloy and solid salt with the enrichment of the alloy in potassium. It is known that sodium and potassium, as well as their alloys, wet salts very readily. The heats of vaporization of sodium and potassium, both very high, are very nearly equal and, there is evidence that the heat of formation of potassium carbonate is slightly higher than that of sodium carbonate. Therefore, as reaction proceeds, there is a slight cooling effect due to the reaction itself which tends to maintain liquid alloy on the surface of the salt particles.

Some earlier investigations, carried out with a small 25" column, in which the temperature controls were by no means as effective as they were in the larger column, are significant in connection with the enrichment mechanism. Reactions were carried out in which 0.5 atom of sodium per mole of potassium carbonate was vaporized and passed into a column of potassium carbonate 25" long. When the reaction was completed, the salt was taken out in sections and analyzed for its content of potassium.

The results are given in Table IX and are shown graphically for experiment P-13 in Figure 1.

[redacted]

TABLE IX

Distribution of K_2CO_3 in Salt Column after Reaction with 0.5 Atom of Sodium per Equivalent of K_2CO_3

Exp. No.	Salt. Temp.	At. % K in Alloy	Distance of Salt Sample from Na boiler, inches							
			1	3	4	5	7	9	10	11
			Mole % K_2CO_3 in Salt							
P13	550	99.4	-	-	-	0.5	-	3.0	-	14.4
P14	600	98.7	-	0.6	-	5.4	-	14.6	-	34.6
P8	650	98.5	0.0	-	0.2	-	9.6	-	44.0	-

Distance of Salt Sample from Na boiler, inches			13	15	16	19	22	23	24
			Mole % K_2CO_3 in Salt						
P13	550	99.4	57.0	85.5	-	94.6	-	-	97.1
P14	600	98.7	44.0	79.2	-	90.8	-	-	97.1
P8	650	98.5	69.5	-	88.2	92.9	94.8	96.1	-

As may be seen from the table and Figure 1, the change from practically pure sodium carbonate to practically pure potassium carbonate takes place within a reaction zone approximately 10" high. Six inches above the boiling chamber, the salt is practically pure sodium carbonate and two inches below the top of the column, the salt contains 97.5 mole percent of potassium carbonate. In a space of six inches (10" to 16" from the boiler), the potassium carbonate content of the salt increases from 7.5 to 87.5 mole percent. It seems clear that, in the case of these experiments, the sodium which was vaporized at a temperature of 550° condensed on a zone of salt in the lower part of the column and that in the major portion of this reaction zone, the salt was at all time wet with metal. The enrichment process consisted in a series of condensations and vaporizations of the metal in the reaction zone. Such a mechanism serves to account for the high enrichment factor of the column. While vapor interacts with the salt in passing

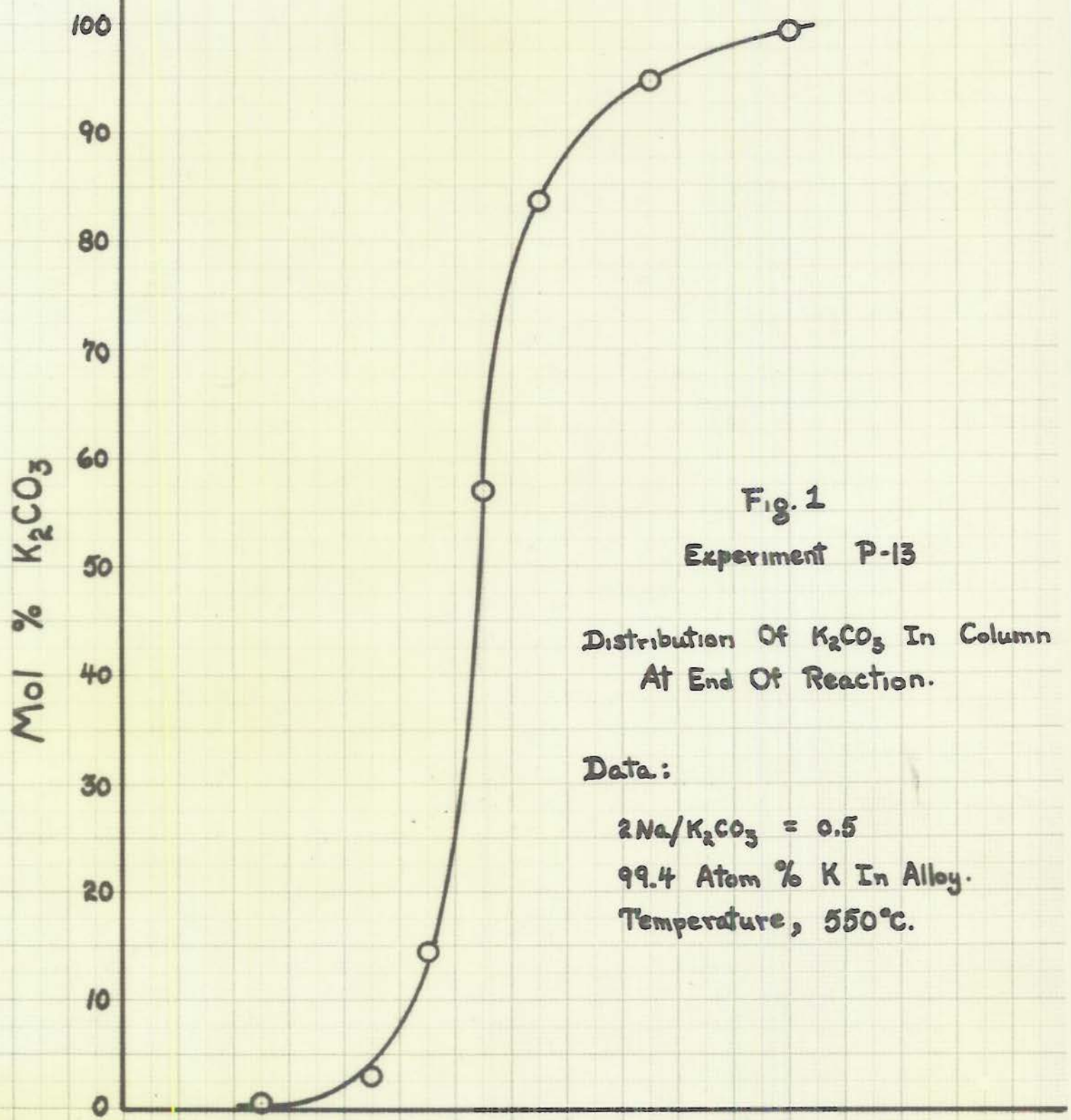


Fig. 1

Experiment P-13

Distribution Of K_2CO_3 In Column At End Of Reaction.

Data:

$2Na/K_2CO_3 = 0.5$

99.4 Atom % K In Alloy.

Temperature, 550°C.

through a column of salt particles, the rate of flow of the vapor is so high that there is not time for the enrichment process to occur to a significant extent.

B. Operation of an Improved Column. The 5.5', 3" column was a stationary one with a boiler attached to one side of the column at the bottom and an arrangement whereby the salt, after completion of the reaction, could be emptied out through the bottom. In order to test the mechanism of the enrichment process, it was necessary to have a column in which excess sodium condensed in the column could run back into the boiler. At the same time, it was necessary to have a column which could be removed from the furnace and emptied. Accordingly, a 40" column of 1-1/2" diameter, which had been used earlier in connection with the experiments recorded in Section III, was set up and provided with temperature controls in three units - bottom, middle and top. The salt in this column rested on a coarse screen which permitted any sodium collecting at the bottom of the column to flow back into the boiler.

Using this column, initial experiments were carried out to determine whether an alloy containing 85 atom percent of potassium could be passed through the column and successfully enriched. In one such experiment, an alloy of 85 atom percent of potassium was passed through the column; the metal which was collected in the receiver was found to melt at 63.2°C. Metallic potassium melts at 63.5° so that the alloy was practically pure potassium. Thereafter, experiments were carried out to determine whether satisfactory alloys might be obtained when as much as 90% of the potassium carbonate was reacted with sodium. The results of such a series of

experiments are given in Table X, where the boiler temperature, which is determined by the back pressure in the condensing system, is given in the second column, the temperature at the bottom of the column is given in the third column and the temperature of the top of the column in the fourth column. In column 5 of the table is given the percent of potassium carbonate reacted and in column 6, the atom percent of potassium in the alloy.

TABLE X

Results with 40" Column; Liquid-Solid Phase Reaction

Exp. No.	Boiler Temp.	Column t at bottom	Column t at top	% K_2CO_3 Reacted	At.% K In Alloy
7	610	615-620	530-515	92	98.0
8	605-615	615-620	505-515	90	98.7
9	605-610	575	495	95	93.4
10	605-615	615-620	525	84	96.1
11	600-615	615	525	84	94.3
12	615	615	500	85	94.9
13	620-625	615	475	92	97.5

As may be seen from the Table, from 84% to 95% of the carbonate was reacted and the alloys obtained from these reactions contained from 93.4 to 98 atom percent of potassium. Some allowance must be made for uncertainties in the temperatures, since the temperatures as recorded were obtained by thermocouples outside the column which had an external diameter of about 2" and which was contained in an alundum core having an internal diameter of 4". Experiment 7 yielded an exceptionally good alloy as did also experiment 8, where 92% and 90% conversion was effected. In all likelihood, the top of the column was somewhat above optimum temperature in most of the experiments. In experiment 13, the top of the column was kept at a temperature of about 475° and an alloy containing 97.5 atom percent of potassium

was obtained with 92% conversion. In these experiments, most of the sodium came off toward the end of the operations, since samples taken of the condensate were liquid (containing less than 90 atom percent of potassium). In order to carry out this reaction, at its best, the column should be provided with a reflux condenser at the top so that liquid potassium could be kept flowing downward over the salt in the column as the process of distillation goes on. It did not seem worth while to carry out such experiments at the time, since it was proposed to construct a new and larger column which had a greater degree of flexibility and control than that described above. This column is now in operation at the Naval Research Laboratory. It may be safely concluded that the effectiveness of a salt column as a means of obtaining a highly enriched alloy, depends upon maintaining the temperature of the salt at such a value that it is constantly covered by a layer of liquid metal.

VI. VACUUM DISTILLATION OF Na-K ALLOYS IN PACKED COLUMN

It seemed worth while to investigate the possibility of obtaining metallic potassium or potassium rich alloys by distillation of less rich alloys in a packed column. If such a column should operate effectively at lower pressures, it might be used in combination with a salt column to effect practically complete separation of potassium from sodium. There are several advantages in operating such a column under reduced pressures. In passing from 800° to 550°, the pressure ratio of the vapors of potassium to sodium is nearly doubled, that is, it increases from 3.3 to 6.4. Moreover, at lower temperatures, corrosion effects are minimized. It was anticipated, therefore, that

[redacted]

at lower pressures, the column would operate with maximum efficiency.

A. Description of Column. The general plan of the column will be evident from Figure 2. The column was constructed of 2" external diameter stainless steel tubing having a wall thickness of 1/16". At the bottom, it was provided with a horizontal, cylindrical boiler approximately 10" long and having an internal diameter of 4". Atthe top, the column was provided with a coil of of 1/8" stainless steel pipe through which air could be blown to condense a portion of the metal vapor and return it to the column. Attached to the condenser was a receiver provided with a number of contact points by means of which the amount of metal collected could be measured as distillation proceeded. Provision was made whereby small samples could be taken for purposes of test. The alloy was injected into the boiler under a pressure of nitrogen. The amount of metal introduced into the boiler was determined by a movable contact point, shown in Figure 2 but not lettered. The temperature of the liquid in the boiler was determined by means of a thermocouple in the thermocouple well A and of the vapor in the boiler by means of a thermocouple in the well O. Thermocouple wells were distributed along the column at intervals of 6", beginning 6" from the bottom of the packing. A thermocouple was provided which could be moved along the outside of the column in order to determine the temperature at any point of the column. Air was passed through the condensing coil at the top at a known rate and the amount of condensation effected was determined by computation from the temperatures of the incoming and outgoing air. The temperature

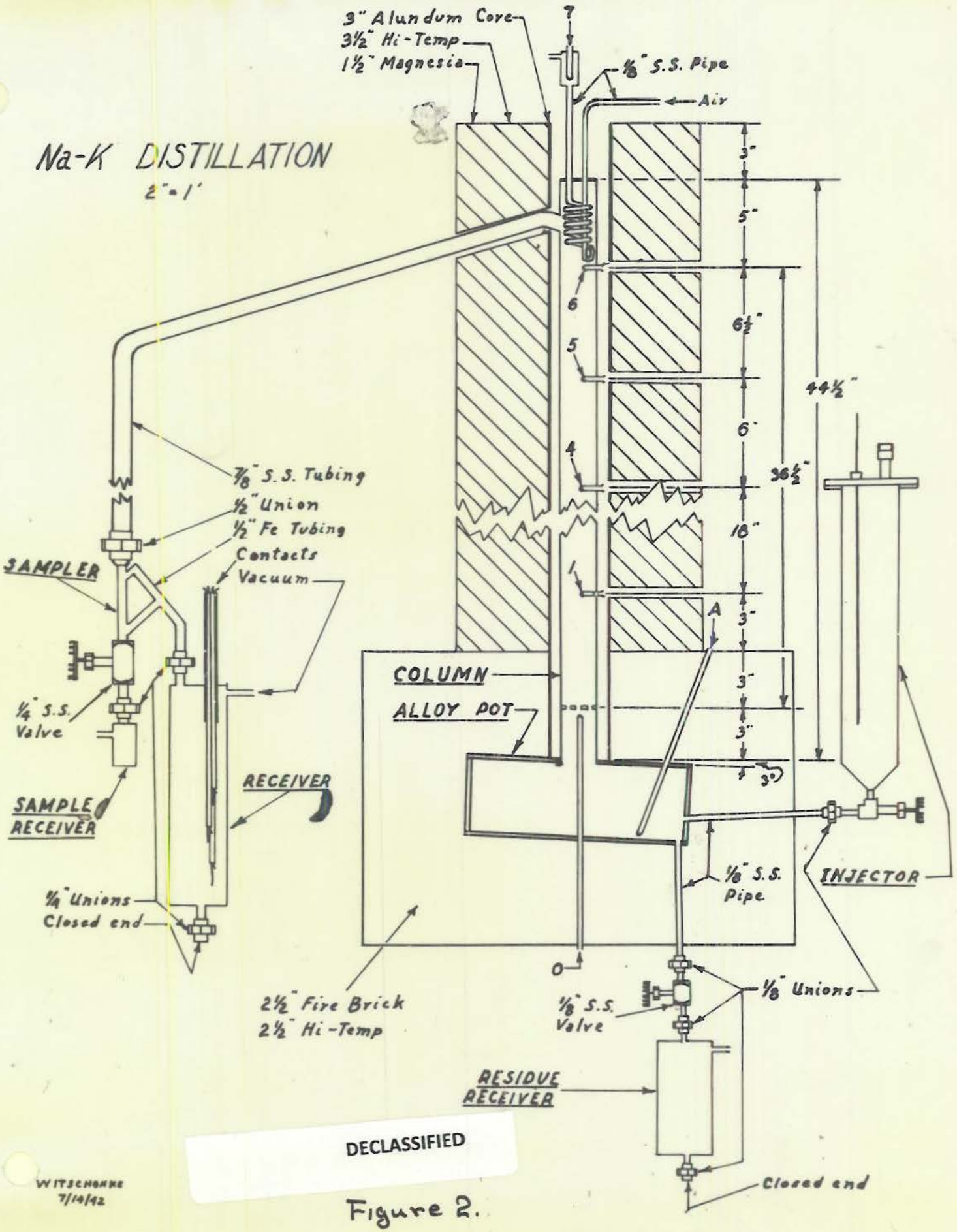


Figure 2.

of the column was controlled by means of 6 coils of Chromel wire wrapped on a 4" alundum core surrounding the column; the boiler was heated by means of two Globar elements. Baffles were attached to the outside of the column to avoid undue circulation of air in the space between the column and the surrounding alundum core.

The packing rings were made of 3/8" lengths of 3/8" O.D. steel tubing of 1/16" thickness. These packing rings rested on a disc which was perforated with 1/4" openings.

B. Operation of the Column. After evacuating the column and filling with nitrogen to a desired pressure, 900 or 1000 cc. of an alloy containing 45 atom percent of potassium were introduced into the boiler. The column was heated to a temperature approximately 25° below the boiling point of potassium at the pressure at which distillation was to be carried out. Once the column had come to the desired constant temperature, the pressure was reduced to the desired value and held constant by means of a manostat. Additional heat was applied to the boiler to vaporize approximately 10 g. of metal per minute and air (approximately 8 cubic feet per minute) was passed through the coil of the reflux condenser.

The temperature of the alloy in the boiler gradually rose until it reached the boiling point of the initial alloy (45 atom percent K). As the vapors rose in the column, the thermocouples distributed along its length indicated when the vapor level reached that point in the column. When the vapors reached the reflux condenser, there was a rise in the temperature of the air flowing through it. The rate of air flow was then reduced to approximately 1 cu.ft./min., which corresponded to the condensation of approximately 4.5 g. of potassium per

minute. Since the heat applied to the boiler was such as to vaporize approximately 10 g. of sodium per minute, this allowed approximately 10 g. of potassium to pass on into the condenser. It may be stated that the heat of vaporization of sodium is approximately 870 cal./g. and that of potassium approximately 460; the molar heats of vaporization are, respectively, 20,000 (25,200) ICT. and 18,000 Calories.

20000

Samples were taken of the initial distillate, as well as of the distillate after the condensation of every 100 cc. of alloy. The composition of the alloy was determined by taking melting point curves. The melting points of these alloys have been carefully checked by chemical analyses in this laboratory; the melting point of pure potassium is 63.5°C. Distillations were carried out at 15 mm., 50 mm. and 100 mm., respectively. The initial alloys in all cases contained 45 atom percent of potassium.

The results are given in Table XI, A,B and C. In the first column, is given the number of the sample taken, in the second, the cubic centimeters of distillate collected up to the point of sampling, in the third, the melting point of the sample and, in the fourth column, the atomic percent of potassium in the distillate.

[redacted]

TABLE XI

Results of K-Na Separation by Means of Packed Column

A. 15 mm. pressure, 1000 cc. of 45 atom % K Alloy

Sample No.	Cc. of Distillate	M.P. of Sample	At. % K of Distillate
1	20	Liquid	<85
2	130	57.6	97.4
3	(240)	62.7	99.6
4	350	-	-
5	(460)	63.3	99.9
6	570	62.9	99.7
7	680	Mushy	20

300 cc. Residues (m.p. - 97°, pure sodium)

B. 50 mm. pressure, 900 cc. of 45 atom % K Alloy

1	10	61.3	98.9
2	120	63.0	99.8
3	230	63.0	99.8
4	340	63.4	100.0
5	450	63.1	99.8
6	560	63.1	99.8
7	670	89.0	2.0

200 cc. Residues (solid but no m.p. taken)

C. 100 mm. pressure, 900 cc. of 45 atom % K Alloy

1	10	Liquid	85
2	120	Mushy	95
3	230	61.8	99.2
4	340	63.4	100.0
5.	450	63.5	100.0
6	560	63.5	100.0
7	670	89.3	2.0

200 cc. Residues (solid but no m.p. taken)

On examining the table, it will be noted that the first two or three samples contained a considerable amount of sodium. The reason for this is that in preceding experiments, sodium vapors were carried into the condensing system of the column and these were not completely removed before starting the next experiment. This sodium, therefore, contaminated the earlier samples but, once this sodium was washed out, later samples

[redacted]

represent correct values.

It is evident that practically complete separation between sodium and potassium was effected at all three pressures. The column operated somewhat more effectively at the higher pressures but, nevertheless, even at 15 mm., the separation was practically complete. The sixth sample taken (Table XI,A) analyzed 99.7 atom percent of potassium and the seventh, 20 atom percent of potassium. The residual metal in the boiler had a melting point of 97° and was pure sodium. At 50 mm. pressure, where 900 cc. of alloy were distilled, a practically complete separation was obtained between samples 6 and 7. Sample 6 had a melting point of 63.1°, corresponding to 99.8 atom percent of potassium, while sample 7 had a melting point of 89°, corresponding to 2 atom percent of potassium. In this experiment, even the earliest samples were practically pure potassium; in this case, the condenser tube had been washed out by boiling pure potassium through the column until the sodium had been practically completely removed.

At 100 mm. pressure, the results were equally satisfactory. Sample 6 had a melting point of 63.5°, which corresponds to pure potassium, while sample 7 melted at 89.3°, which corresponds to 2 atom percent of potassium.

The recovery of potassium in the second and third distillations was practically complete; the recovered potassium weighed 465 g. as against 456 g. computed from the weight of the original alloy. Volume measurements were not better than several percent.

A better idea of the efficiency of the column may be gained by examining the temperatures at different points in the column

as distillation proceeded. The temperature records of the various thermocouples in the column (indicated on Figure 2) are shown on plates 1, 2 and 3. On plate 1, are shown the records of the thermocouple A in the boiler liquid, the thermocouple O in the boiler vapor and the thermocouple 1 in the column at a point 6" above the boiler. On plate 2, are shown the records of thermocouples 2, 3 and 4, located at 12", 18" and 24" from the boiler and on plate 6, are shown the records of thermocouples 5 and 6 located 30" and 36" from the boiler. Couple No. 6 is right at the top of the packing and indicates the temperature of the effluent vapors. For purposes of comparison, the boiling temperatures for potassium, sodium and 45 atom percent of potassium alloy are given for 15, 50 and 100 mm. pressure, in Table XII.

TABLE XII

Boiling Points of Potassium, Sodium and 45 at. % K Alloy

Pressure	Potassium	Sodium	45 At.% K Alloy
15 mm.	465°C	575°C	500°C
50 mm.	535°C	625°C	575°C
100 mm.	580°C	700°C	625°C

Turning to plate 1, boiling began at a point indicated on the plate where the same temperature was recorded by the thermocouples A and O. As distillation continued, these two couples recorded practically the same temperature and at the end of thirty minutes, the temperature began to rise gradually as distillation proceeded. The first sample of 10 cc. was taken off 23 minutes after boiling began and a total of 120 cc. had distilled when the second sample was taken off at the end of 32 minutes. At the end of 78 minutes, when sample 6 was taken off, the temperature of the boiler and vapor had

reached 700°, which is the boiling point of sodium, under a pressure of 100 mm. Sample 7, which consisted of practically pure sodium (2 at. % K), was taken off at the end of 92 minutes.

Thermocouple 1, whose record is shown on plate 1, reached a temperature of 575°, the boiling point of metallic potassium, a few minutes after boiling began and maintained this temperature until at the end of 63 minutes, when sample 5 was taken off. From this point onward, the temperature of thermocouple 1 rose slowly for about 5 minutes and then more rapidly until, at the end of 78 minutes, when sample 6 was taken off, its temperature was 685°, only a few degrees below that of the boiler. From this point onward, couple No. 1 recorded a temperature ranging from 685° to 695° until the run was completed.

Turning now to plate No. 2, on which appear the records for thermocouples 2, 3 and 4, it will be observed that as potassium vapor rose in the column, the temperature of the couples, at intervals of a few minutes, rose, one after another, to 575°, the boiling point of potassium. This temperature was maintained by all three couples until sample 6 was taken off at the end of 78 minutes. Just shortly before this time (4 minutes), the temperature of couple 2 broke sharply and its temperature, in less than one minute, rose from 575° to 675°; couple No. 3 followed just a few minutes later, shortly before the sample was taken. The temperature of couple No. 4 rose sharply to 675° just a minute or two after sample 6 was taken. All three couples maintained a temperature in the neighborhood of 675° until the run was completed. Considering now, plate 3, bearing the records of couples Nos. 5 and 6, the temperature of No. 5

rose to 575° some 8 minutes after the sodium began to boil and couple No. 6 rose to the same temperature some 4 minutes later. Thereafter, both couples maintained a temperature of 575° until, at the end of 83 minutes, the temperature of couple No. 5 rose sharply to 690° and couple No. 6 followed about 2 minutes later. Both couples maintained a temperature of 690° until the run was completed when sample No. 7 was drawn off.

Bearing in mind the results recorded in Table X, according to which sample No. 6 consisted of pure potassium and sample No. 7 of practically pure sodium, it is apparent that when sample No. 6 was drawn, the potassium had been almost completely separated from the sodium. At the point of couple No. 4, 12" below the top of the packing, the temperature was still 575°, as recorded on plate 2. About 5 minutes were required for the sodium to heat up the packing and the enclosing cylinder between couples 4 and 6. The sodium vapors at a temperature of about 700° reached thermocouple No. 5 in 3 minutes and about 2 minutes later, thermocouple No. 6. Subsequent to this time, some 7 minutes, practically pure sodium was distilled out of the column. This was collected as sample No. 7 which had a melting point of 89.3° and contained only 2 atom percent of potassium.

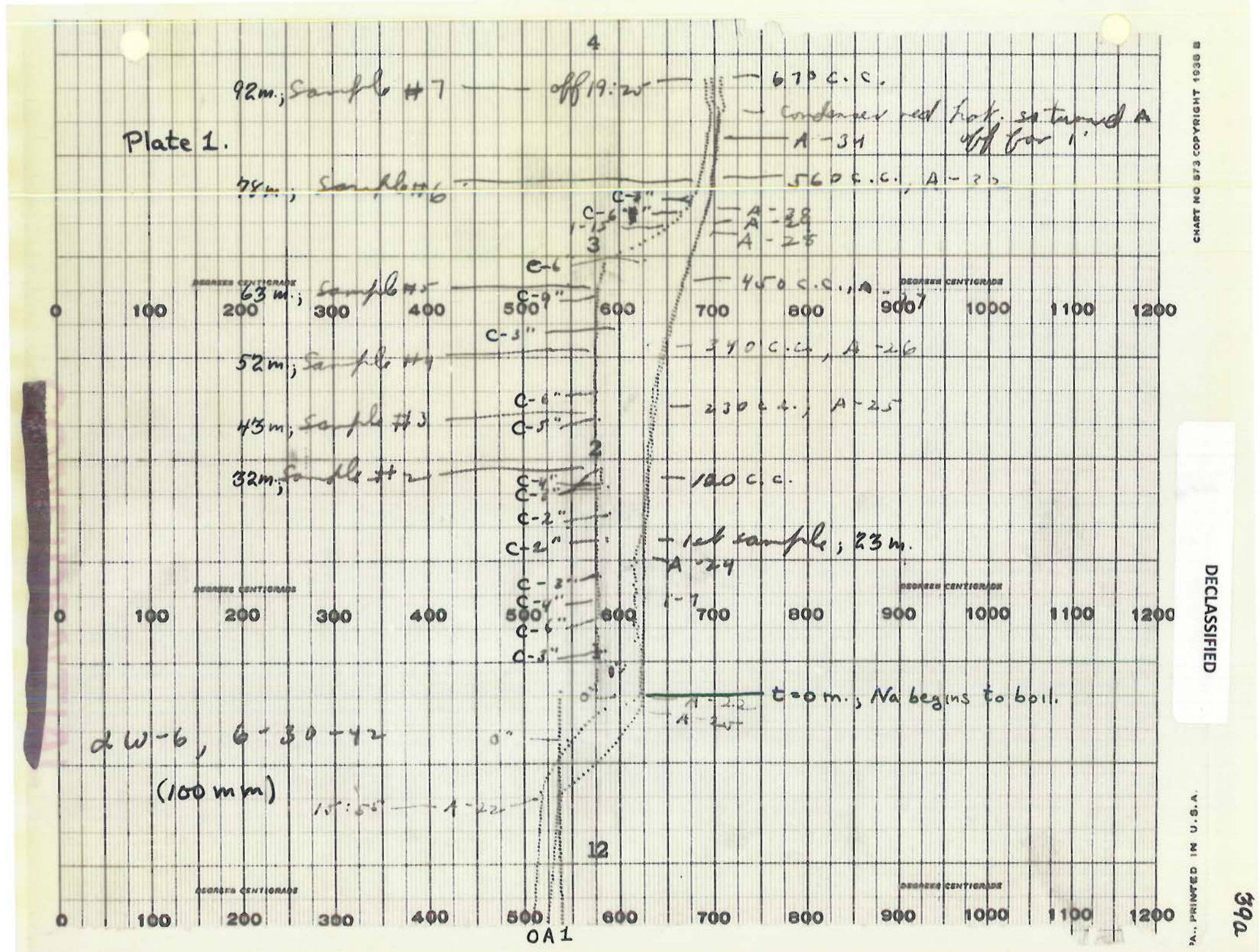
It will be noted that the only couple which showed a gradual rise of temperature as the distillation process approached completion, was thermocouple No. 1, located in the packing 6" above the boiler. In the case of all other thermocouples, the temperature rise was abrupt from 575° to above 675° in 2 minutes, or less. This means that, as the metal in the boiler became very rich in sodium, the separation took place, for the most part, within the first 6" of the packing; certainly in less than 12"

[redacted]

of the packing. It would seem, therefore, that a packed column 12" in length would be adequate for separating potassium from sodium.

Some further evidence as to the surprising efficiency of the column is afforded by the temperature recorded by thermocouple No. 8 whose position could be changed, at will, to any point of the column. This thermocouple was not connected to the recorders at all times but was cut in from time to time; the record of its temperature is shown on plate 1. The points shown on the plate as C, 2-9, are the temperatures recorded at distances ranging from 2" to 9" from the bottom of the cylindrical column or from 1" below the packing to 6" above. Points marked C-2, with the couple just below the packing but outside the column, show a temperature of approximately 580°, some 15° above the temperature of couple No. 1 which is at the temperature of boiling potassium. At C-3, which is right at the bottom of the packing, the temperature is from 5° to 10° above that of couple No. 1. At positions C-4 and C-5, which are, respectively, 1" and 2" above the bottom of the packing, the temperatures recorded are just slightly above 575°. At C-6 and C-9, thermocouple No. 8 recorded temperatures practically the same as those of thermocouple No. 1. After taking off sample 5, the temperature recorded at C-6 is at first slightly above that of couple No. 1 and thereafter is practically the same as that of couple No. 1.

The conclusion to be drawn from the variation of the temperature of couple No. 8, at its different positions, is that, in the early part of the distillation process, while the alloy was still relatively rich in potassium, the fractionating process was completed in about 3" of packing. However, as the alloy in



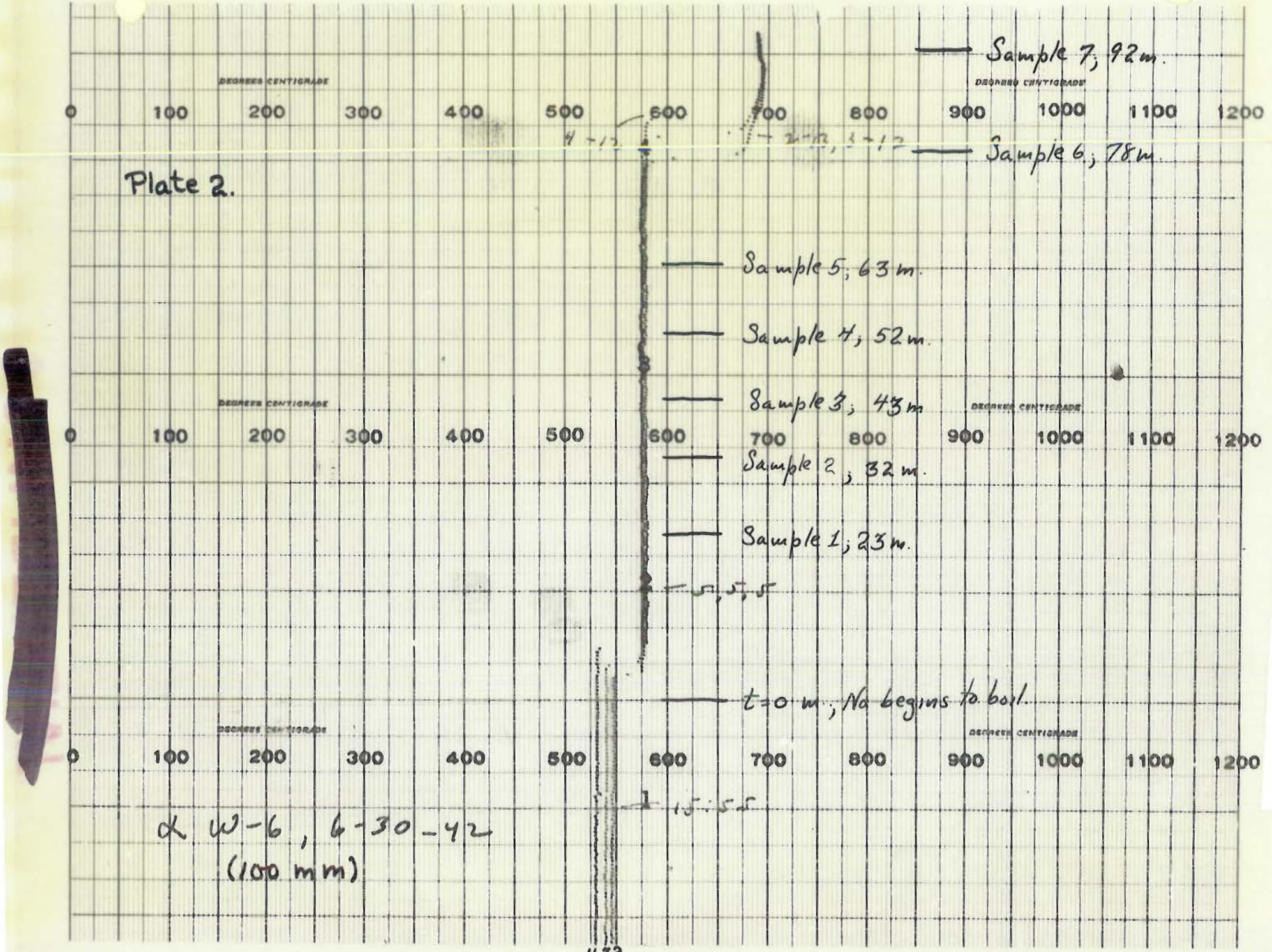
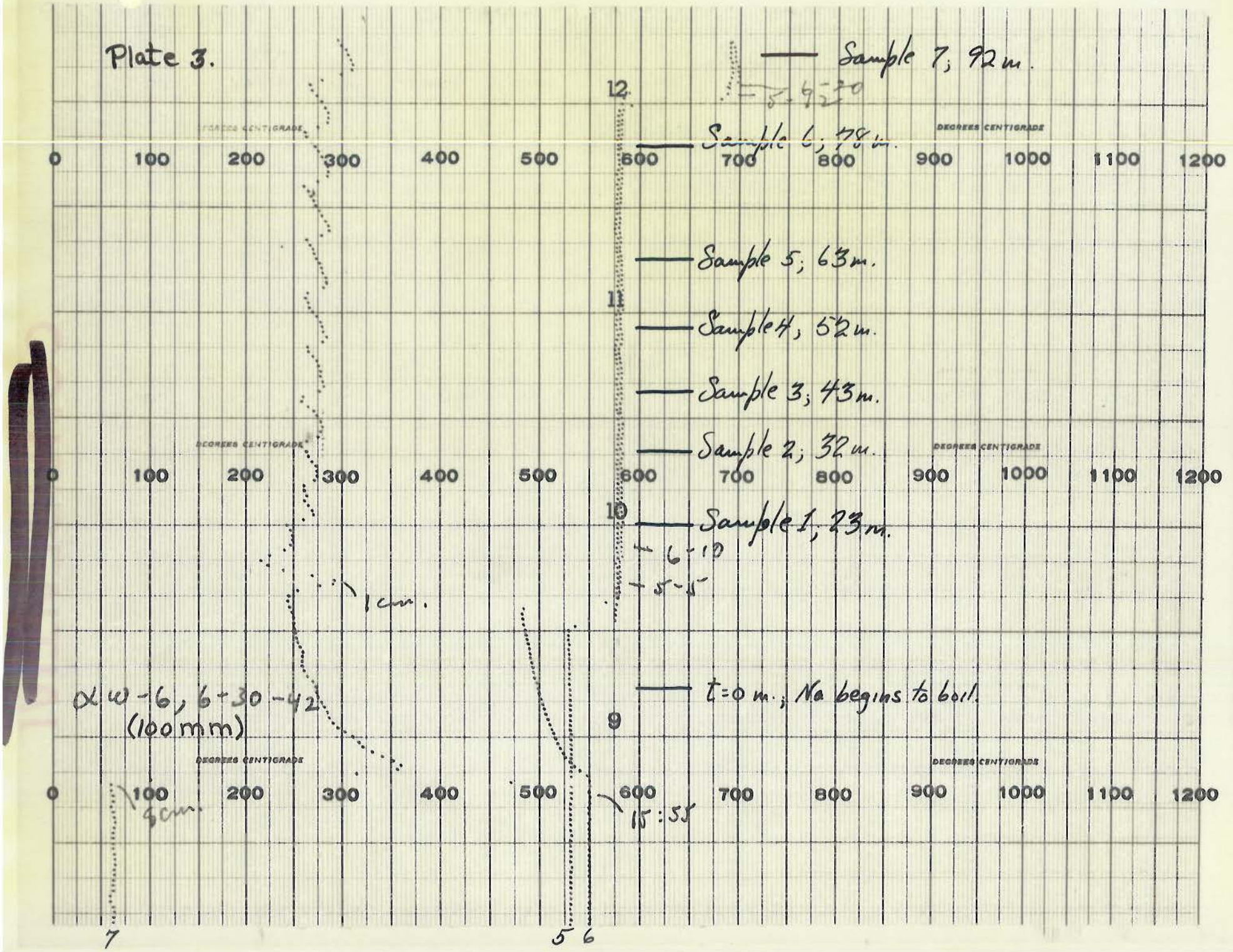


Plate 2.

α W-6, 6-30-42
(100 m m)



the boiler became depleted of potassium, it required a greater length of packing to effect the separation. But even in the extreme case, where the potassium content of the alloy had reached extremely low values, not more than 12" of packing was required to effect complete separation of the two metals.

VII. POSSIBLE CONTINUOUS PROCESS WITH A SALT COLUMN

A. Salt Flow Method. Since favorable reaction occurs when sodium vapor is carried upward through a column of solid salt, such as potassium fluoride or potassium carbonate, it seemed possible that a continuous process might be developed in which the solid potassium salt was fed into the column at the top and the resulting sodium salt was removed from the column at the bottom. It was to be expected that some difficulties would be experienced in carrying out such a process under vacuum but it appeared that these difficulties might not be insuperable. However, another difficulty is present which definitely precludes such a process where a pure salt is employed.

All salts possess the property of becoming tacky at a temperature in the neighborhood of 0.6 of the absolute temperature of their melting points. Thus, potassium carbonate, which melts at about 860°C, becomes tacky at about 400°C. The particles of potassium carbonate stick together above 400° although, when the temperature is lowered below 400°, they lose their tackiness and again are capable of flowing freely through a tube. It was thought that the difficulty might be overcome by mixing a non-tacky material, such as magnesium oxide, with the salt. The presence of magnesium oxide does not interfere with the reduction of potassium carbonate by means of sodium.

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Results are given in Table XII for reductions in a 40" column of mixtures of potassium carbonate with 25 and 50 weight percent of magnesium oxide, respectively. In these experiments, 0.5 equivalents of sodium was added per equivalent of potassium carbonate. As may be seen from the table, the alloys obtained were quite satisfactory.

TABLE XII

Reduction of K_2CO_3-MgO Mixtures

Na_2/K_2CO_3 = 0.5; t = 625°C; back pressure = 15 mm.

A. 4-6 mesh, 25 wt. % MgO

Exp. No.	At. % K in Alloy	Minutes per 100 g. Na
86	99.1	40
87	97.2	36

B. 4-6 mesh, 50 wt. % MgO

88	99.5	40
89	99.4	36
90	99.2	45
91	98.9	49
92	98.6	36

An experimental column, provided with suitable loading and unloading devices was constructed and the flow of potassium carbonate containing 50 weight percent of magnesium oxide was tested out up to temperatures of 550°C. Although the salt particles in this case were much less tacky than were those of pure salt, nevertheless, they did not flow satisfactorily through the column when hot. It seems doubtful that a process can be developed along these lines which will operate successfully. By increasing the magnesium oxide content of the salt still further, a point could probably be reached where the particles would flow and reductions could be carried out satisfactorily by means of sodium but the cost of such an operation would be high because of the

low volume yield of metal and the necessity of recovering the magnesium oxide from the spent salt.

The particles of mixed K_2CO_3 and MgO were prepared by mixing the two in powder or finely divided form, wetting with water, partially drying at 130°C, crushing and classifying and thereafter drying at 600° or higher. Magnesium oxide retains its water at temperatures where potassium carbonate is completely dehydrated. The oxide does not dehydrate readily, even at fairly high temperatures, and, in practice, it would probably be necessary to heat the salt to an elevated temperature for a considerable length of time, perhaps, in a vacuum. It was concluded that a continuous process of this type is not practicable at this time.

B. Moving Pot Method. Another possible method of passing salt along a column through which sodium vapor is carried in reverse direction consists in passing through the column a series of cylindrical containers filled with salt particles, each container being open at the top and closed at the bottom with a screen of coarse mesh. If containers of this type could be carried through a hot column while metal vapors were passed upward through the column, the potassium salt could be successfully reduced. The clearance between the containers and the column may be considerable without influencing the efficiency of the column.

This type of column was tested out by introducing six 6" containers into a 1.5" column approximately 36" long. The column was provided with a boiler at the bottom and the clearance between the containers and the column was gradually increased and the effect of the clearance on the composition of the alloy was

determined. The results are given in Table XIII.

TABLE XIII

Effect of Wall Clearance on Composition of Alloy

Na_2/K_2CO_3 = 0.50; t = 625° C; back pressure = 15 mm.;4-6 mesh

Exp. No.	Wall Clearance	At. % K in Alloy	Minutes per 100 g. Na
96	0.001"	98.2	31
97	0.002	98.6	51
98	0.003	97.8	55
99	0.006	98.3	64
100	0.012	96.9	55

As may be seen from the table, even with a wall clearance of 0.12", an alloy of satisfactory composition was obtained. The inner diameter of the column was 1-1/2"; if a column of larger diameter were employed, greater clearance allowance would be permissible. The difficulty with any such continuous process is largely the mechanical one of introducing and removing the salt containers while maintaining vacuum in the column at elevated temperatures. This approach to the solution of the problem of the continuous operating column was discarded as being impractical at this time.

VIII. K_2S BY REDUCTION OF K_2SO_4

As mentioned in the report of September 1, 1941, potassium may be obtained by reduction of potassium sulfide by means of sodium at lower temperatures or by means of iron, aluminum and magnesium at higher temperatures. One of the chief difficulties in connection with this method is the fact that potassium sulfide is not produced commercially and a method of producing potassium sulfide of a high degree of purity by the reduction of potassium sulfate has not as yet been developed.

The reduction of potassium sulfate was studied at some length.

Fairly satisfactory reduction may be carried out with carbon, using iron as catalyst, at temperatures in the neighborhood of 1100°C. Using carbon monoxide and carbon, with a suitable catalyst, considerable reduction is obtained in the neighborhood of 1000°C. The use of a certain amount of hydrogen along with carbon monoxide, facilitates the reduction of potassium sulfate; the temperature of the initial reduction falls as low as 800°C but complete reduction cannot be effected at that temperature. In no case, was it found possible to obtain a thoroughly satisfactory product by the reduction of potassium sulfate. Seemingly, a certain amount of sulfate remains unreduced, or, if hydrogen is used in connection with the reduction process, a certain amount of hydrolysis takes place and potassium hydroxide is formed. By treating such a product with a considerable excess of sodium, all the potassium may be distilled out of the salt, but a considerable amount of sodium is lost in the process, apparently, in reducing residual potassium sulfate.

Potassium sulfide is not a convenient salt to handle. It is extremely sensitive to moisture, giving off hydrogen sulfide, and it oxidizes and, indeed, ignites in air when pure. In a molten condition, it is extremely reactive toward almost all metals and the problem of a container for a salt such as potassium sulfide becomes a very difficult one. In certain of the reductions, a graphite liner was employed to protect the metal containers. In view of these facts, potassium sulfide is considered to be impractical in a commercial process for the production of metallic potassium under present circumstances.

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IX. SPRAY GUN METHOD OF OXIDIZING POTASSIUM

Metallic potassium, as well as sodium-potassium alloys, have been successfully oxidized at the Naval Research Laboratory by passing a slow stream of nitrogen over the metal heated to a temperature just below its boiling point. The Mine Safety Appliance Company has been oxidizing potassium by spraying the metal into a dry air chamber with a spray gun. This method would be the most convenient and economical if it served to convert the metal completely into its highest oxide.

Several series of experiments were carried out with alloys containing between 38 and 98 atom percent of potassium. In carrying out the oxidation, the metals were sprayed into an enclosed chamber through a De Vilbiss spray gun by means of air at pressures between 40 and 60 pounds. The air was dried by means of silica gel towers and had a negligible moisture content. Arrangements were made for heating the air that operated the gun. The air, as it entered the gun, could be heated as high as 350°. The metal could be heated to 150°; it was necessary to heat the metal to a sufficiently high temperature to maintain it in a suitably liquid condition. The burning chamber was surrounded with an air jacket through which air could be circulated and the interior temperature controlled. Samples were taken of the air in the chamber to determine its oxygen content during the process of burning. Samples were taken of the oxides and their oxygen content was determined. This served to show to what extent the metals had been converted to their highest oxides (Na_2O_2 and K_2O_4).

In the first series of experiments, most of the alloys had a composition in the neighborhood of 70 or 77 atom percent of potassium. The results are given in Table XIV.

TABLE XIV

Results of Burning K with Spray Gun

Exp. No.	At. % K in Alloy	Lbs. burned per hour	Air Temp.	Burning Chamber Temperature	Cc. O_2 per g. oxide
7	68.8	17.5	30	>200	200
8	68.2	6.3	30	180	195
9	54.4	6.1	60	190	190
10	67.2	6.7	240	210	202
11	72.0	5.0	300	190	206
12	69.9	9.0	300	230	210
13A	38.4	4.8	28	170	172
13B	38.4	3.1	150	130	174
14	70.0	5.8	350	200	208
16	77.1	6.9	250	220	210
17	76.5	2.6	250	120	204
18	78.7	5.0	300	160	208
19	84.7	4.5	250	195	214

The atomic percent of potassium in the alloy is given in the second column; the rate at which the metal was burned in the third column; the temperature of the air entering the spray gun in the fourth column, the temperature in the burning chamber in the fifth column and the oxygen content of the oxide, in cubic centimeters of oxygen per gram of oxide under normal conditions, in the last column.

For convenience in evaluating the results, the oxygen content of various mixtures of Na_2O_2 and K_2O_4 is given in Table XV.

TABLE XV

Mole % K_2O_4 in oxide	38	54	70	77	85	95
Cc. of O_2/g.oxide	182.6	207.0	219.1	223.4	226.6	234.0

As may be seen from Table XIV, the conversion of the metals to their highest oxides was in all cases incomplete. Alloys having a potassium content in the neighborhood of 70 atom percent of potassium yielded from 200 to 210 cc. of oxygen as against 219 cc. required for complete conversion. Alloys containing 38 atom percent of potassium yielded 172 and 174 cc. of oxygen

as against 182.6 cc.,theoretical. Alloys having a potassium content in the neighborhood of 77 atom percent yielded an oxygen content ranging from 204 to 210 cc. as against 223.4 cc. for complete oxidation. An alloy containing 84.7 atom percent of potassium yielded 214 cc. of oxygen per gram of oxides as against 226.6 cc., theoretical.

It was thought that the deficiency of oxygen might, in the main, be due to incomplete conversion of sodium to Na_2O_2. However, when richer alloys were burned, it became clear that the oxygen deficiency was, at least in part, due to incomplete oxidation of the potassium, since the oxygen content of the resulting oxides ran below that required if the potassium had all been oxidized to K_2O_4 and the sodium to Na_2O.

In order to eliminate the influence of sodium, a second series of experiments was carried out in which the potassium content of the alloys ranged between 93 and 98 atom percent. The results are given in Table XVI.

TABLE XVI

Oxidation of High Potassium Alloys

Exp. No.	At. % K in Alloy	Lbs.burned per hour	Air Temp.	Burning Chamber Temperature	Cc.O_2 per g. oxide
20	98	7.9	200	200	224
21	94	7.9	175	200	218
22	95	6	250	200	225
24	93	-	210	200	218
25	97	-	215	150	223
26	95	4.8	125	170	215
27	95	7.2	130	200	219
28	95	4.9	125	165	213
29	96	8.1	120	190	220
30	93	3.5	120	130	199
31	93	8.0	105	135	201
32	93	5.7	115	150	205
33	93	5.5	125	150	207

An alloy containing 95 atom percent of potassium, if completely

converted to K_2O_4 and Na_2O_2 would yield a product capable of producing 234 cc. of oxygen per gram of mixed oxides. A variation of the potassium content by several atomic percent would affect the oxygen content by only a few cubic centimeters. As may be seen from an inspection of Table XVI, oxidation, in all experiments, was far from complete. The highest value obtained was 225 cc./g., in experiment 22, a deficiency of 9 cc. Depending upon the conditions of burning, the oxygen content of the oxides obtained in various experiments ranged to values as low as 199 cc./g. In general, it seems that the oxygen content of the oxides is the higher the more rapid the rate of burning, the higher the temperature of the air through the gun and the higher the temperature in the burning chamber. For example, in experiment 7 of Table XIV, where the burning rate was 17.8 lbs./hr., the oxygen content from a 68.8% alloy was 200 cc., while in experiment 8, carried out under practically the same condition with a lower burning rate, the oxygen content was 195 cc. The highest oxygen content obtained with a 70% alloy was 210 cc., in experiment 12. Here, the air passed through the gun had a temperature of 300°C and the temperature of the burning chamber was 230°C.

Examining table XVI, it will be noted that in experiments 30 to 33, inclusive, where the air temperature was in the neighborhood of 120° and the temperature of the burning chamber ranged from 130° to 150°C, the oxides were all of very low oxygen content, ranging from 199 to 207 cc. The best result was obtained in experiment 22 where the air temperature was 250°C and the burning chamber temperature was 200°C. In experiments 26 to 33, inclusive, the spray gun employed was identical

with that used by the Mine Safety Appliance Company. In fact, in all these experiments, the conditions of operation were practically identical with those used by M.S.A.C.

The conclusion to be drawn from these results is that potassium, when burned in a spray gun, yields oxides in which the metal is not completely converted to K_2O_4 and that, in general, the degree of oxidation is the higher, the higher the temperatures at which the metal is burned. That the potassium was not completely converted to K_2O_4 in these experiments was conclusively shown by subjecting samples of the oxide to the action of pure oxygen under controlled conditions. From 100° upward, the oxides absorbed oxygen with considerable readiness. The rate slowed up as time went on and was greatly accelerated on raising the temperature. Between 150° and 200°, the absorption of oxygen was rapid. It was not found possible, however, to carry the oxidation completely to K_2O_4. Probably, this was due to the fact that,as the temperature of the oxides was raised to accelerate the rate of oxidation, the material sintered and became less porous, thereby decreasing the rate at which oxygen could diffuse into the interior of the particles of incompletely oxidized material.

The following results are typical: In experiment 24, the original oxide analyzed 218 cc. of available oxygen per gram. After heating in an atmosphere of oxygen at 150° for 21 hours and at 200° for 6 hours, its oxygen content was raised to 227 cc./g. an increase of 9 cc./g. The oxides from experiment 25 yielded, initially, 223 cc./g., after heating in an atmosphere of oxygen at 175°C for 17 hours, its content of available oxygen was raised to 228 cc./g., an increase of 5 cc./g.

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It would seem worth while to study the oxidation of potassium by the spray gun method further, since it offers a most convenient method of converting the metal. It is probably not practicable to raise the temperature of the air above 250° or 300°, since, even at these temperatures, the rate of erosion of the spray gun tips is high. Possibly, by using certain of the platinum metals, more resistant tips might be made which would withstand a higher temperature but, even so, it is doubtful if a satisfactorily high burning temperature may be obtained by this means. A more promising method would be to increase the oxygen content of the air. It would be quite possible to raise the oxygen content as high as 40%, or even higher, in which case, the temperature of the flame beyond the gun would be raised considerably. In certain of the earlier experiments, particularly in experiment 7, as much as 10% of the oxygen in the chamber was used up. In the later experiments recorded in table XVI, the oxygen content did not fall below 17%. By increasing the oxygen content of the air and decreasing its rate of flow, the concentration of oxygen in the air within the chamber would be kept in the neighborhood of 20% to 25% and the temperature of the flame should be greatly increased. This should favor the production of the highest oxides.

V. CONCLUSION

Metallic potassium can be produced as pure metal or as an alloy with sodium according to a number of different processes. Some of these methods are impractical at this time because of scarcity of essential materials, while others involve unduly high tempera-temperatures. Taking everything into consideration, the

reduction of potassium carbonate in the solid state by means of metallic sodium seems to be much the most promising reaction. By combining the potassium carbonate column with a short packed column, practically pure potassium can be obtained with a conversion of potassium carbonate that runs well over 90 percent.

Dry potassium carbonate is available commercially at about 6.5 cents per pound and sodium sells for about 15 cents per pound, but can be produced in quantity at a much lower figure. There is an overproduction of sodium at the present time and this will probably continue while the war lasts. The potassium carbonate process would, thus, appear to be one which could be put into operation quickly in case of need. It should not interfere with the production program except as alloys are required to build the reactor units.

On the basis of theoretical yields, the cost of potassium carbonate (at 6.5 cents) per pound of potassium is 12.8 cents and the cost of sodium (at 15 cents) is 8.8 cents, making the total cost of materials 21.6 cents per pound of potassium. Assuming that the efficiency of the process is 90%, which seems reasonable in the light of experience, the cost of materials per pound of potassium would be 23.8 cents.

Against this cost should be credited the value of the sodium carbonate which is produced. This might amount to as much as 2 cents per pound of potassium. The net cost of material should thus run in the neighborhood of 22 cents per pound of potassium. If the process were carried out on a large scale, the cost of sodium should be figured at a value much below 15 cents per pound.

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Costs, other than those of materials, cannot well be estimated at this time. Once the pilot unit is in operation at the Naval Research Laboratory, it should be possible to arrive at a reliable figure for the over-all cost of potassium by the carbonate process.

The problem of converting the metal to the oxide may be touched upon briefly. This problem was studied only incidentally in connection with the problem of producing the metal. There are two methods available for oxidizing potassium: (1) that developed at the Naval Research Laboratory, in which nitrogen is passed over the metal at a temperature just below its boiling point and the vapors are passed through a hot nozzle into air, where they burn. (2) A process developed by Mine Safety Appliance Company in which the molten metal is atomized in a spray gun and burned in air.

Neither of these two methods operates satisfactorily in all respects. The difficulty of the first method is that the burning nozzle corrodes excessively and must be replaced at frequent intervals. Another inherent disadvantage lies in the fact that the metal must be heated and vaporized. The rate of burning by this method is rather low and the cost for labor would probably run rather high.

The spray gun method of burning potassium to the oxide seems very attractive. The rate of burning is high, it requires little attendance, and there is no charge for heating and vaporizing the metal. The difficulty is that the metal is not completely oxidized to K_2O_4. It has been stated that potassium has been successfully burned by the spray gun method

by Mine Safety Appliance Company, but I have no independent evidence on this point. Our own experience has indicated that potassium is incompletely burned to K_2O_4 with a spray gun under ordinary conditions. The problem should be studied further. In particular, the metal should be burned in air of higher oxygen content where higher flame temperatures would be obtained.

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Brown University,
Providence, R.I.
September 1, 1942

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