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AN ANCIENT VOLCANIC ERUPTION IN THE UPPER YUKON BASIN.

By STEPHEN R. CAPPS.

It has long been known that a large area in Alaska and Yukon Territory is covered by a layer of volcanic ash. The ash lies near the surface, beneath a thin covering of soil or silt, and gives evidence of an explosive volcanic eruption that in terms of geologic history is very recent, though antedating historic record in this part of the world. The first published description of this material is that given by Schwatka,¹ who observed the ash layer along the banks of Lewes River and its headward tributaries in 1883. In 1887 Dawson² extended the known area of the ash and estimated its total area, the direction from which it came, and the approximate length of time since it was deposited. In 1891 Hayes,³ in company with Schwatka, conducted an exploration from Fort Selkirk, on the Yukon, to the Copper River basin. They traveled westward into an area in which the ash gradually increased in thickness to its maximum near the international boundary and rapidly thinned west of that line. In 1898 and 1899 Brooks⁴ explored the headwaters of White and Tanana basins and made many observations on the areal distribution and thickness of the ash. The present article is based largely upon information personally obtained or collected by Mr. Brooks. The writer first became interested in this occurrence in 1908, when working in the Nabesna and White River district,⁵ and a second expedition into the same general region in 1914 gave opportunity for a more extended study of the ash fall. Records of the outer limits of the ash-covered area have been taken from many sources, especially from the published and unpublished notes of the members of the Geological Survey of Canada and of the United States Geological Survey.

The general outlines of the ash fall are shown on figure 23, the relative thickness of the deposit being indicated by contours. The outer limits of the area are drawn to include all points at which the ash has been observed and at which it is still recognizable as a distinct layer. Without question a thin film of dust could at the time of the eruption have been observed over an enormously greater area than that here outlined, but, as will be shown, the ejection of the ash antedates recorded history in America, and the area affected can now be determined only by the presence of the ash that has been preserved. Less than one-fourth inch of ash falling at the time of this eruption over a vegetation-covered upland would probably be insufficient to form a layer that would now be generally recognizable.

The outermost observations recorded include, on the west, observations on Nabesna, Tanana, and Yukon rivers, by Brooks and others; on the northeast and east, on Gravel, Macmillan, and Pelly rivers, by Keele, Dawson, and McConnell; on the southeast, on Teslin River and at Lakes Marsh and Bennett, by Schwatka, Dawson, and others; and on the south and southwest, along the southeast flank of the St. Elias Range, by Hayes, Brooks, and the writer.

The ash usually appears along the cut banks of the rivers as a thin white band near the top of the bank, covered by only a few inches or a foot or two of soil, silt, or vegetable humus. It is remarkably persistent and is in places continuously exposed for miles. Over any given

¹ Schwatka, Frederick, *Along Alaska's great river*, Cassell & Co., New York, 1885.

² Dawson, G. M., *Report on an exploration in the Yukon District, Northwest Territory, and adjacent northern portion of British Columbia*: Canada Geol. and Nat. Hist. Survey Ann. Rept., vol. 3, pt. 1, pp. 43 B-46 B, 1889.

³ Hayes, C. W., *An expedition through the Yukon district*: Nat. Geog. Mag., vol. 4, pp. 146-150, 1892.

⁴ Brooks, A. H., *A reconnaissance in the White and Tanana river basins, Alaska, in 1898*: U. S. Geol. Survey Twentieth Ann. Rept., pt. 7, p. 475, 1900.

⁵ Moffit, F. H., and Knopf, Adolph, *Mineral resources of the Nabesna-White River district, Alaska, with a section on the Quaternary* by S. R. Capps: U. S. Geol. Survey Bull. 417, pp. 42-44, 1900.

district of small area the ash tends to be rather uniform in thickness, although locally it thickens into lenses or thins out entirely. It occurs prevailing in a single layer, was apparently ejected during one period of eruption, and fell as one continuous shower in which there were no time breaks of sufficient length to interrupt the vertical continuity of the deposit. At a few localities two or more ash beds, one above the other, separated by beds of soil or silt, have been observed, but the sporadic nature of these occurrences and the great preponderance of areas with but a single layer indicate that where two or more superposed layers occur the upper layers are composed of ash derived by erosion from the lowest one and deposited later by wind or by streams. The evidence, therefore, is strongly in favor of but a single period of eruption.

The ash bears a close relation to the present topography, occurring not only over the valley floors of the present stream basins but also over the intervening hills and ridges. Shallow excavations on hillsides and in valleys everywhere reveal its presence. Burrowing animals,

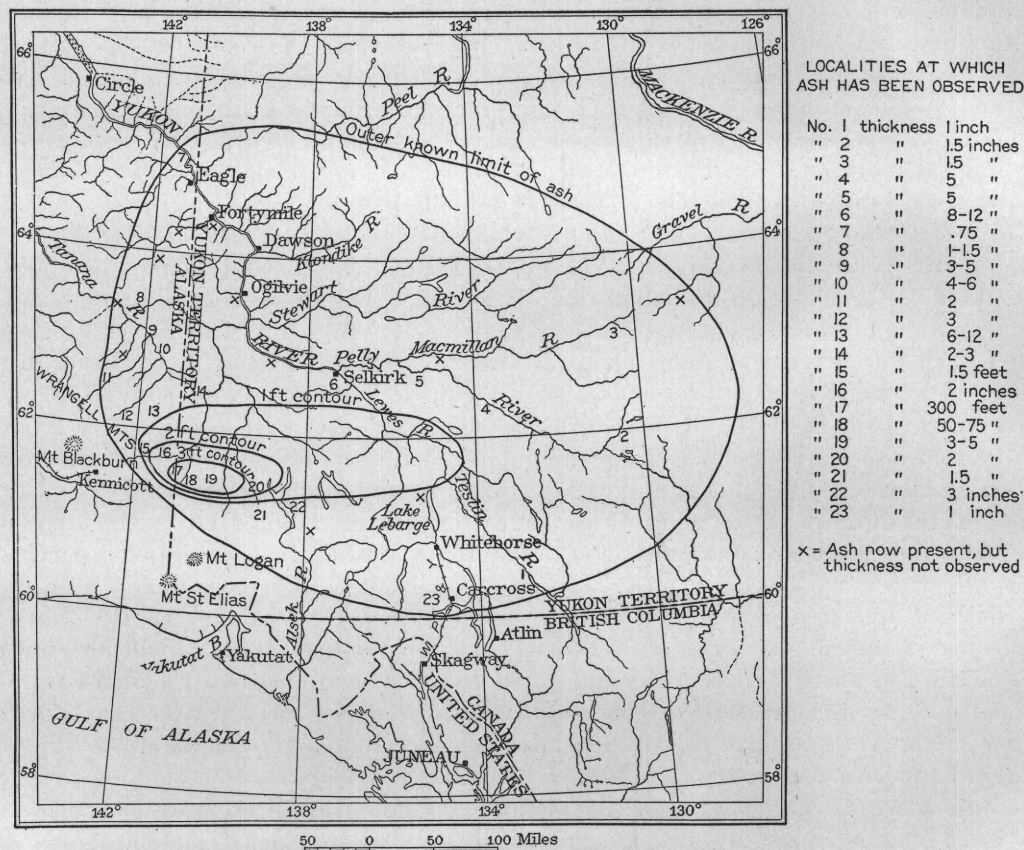
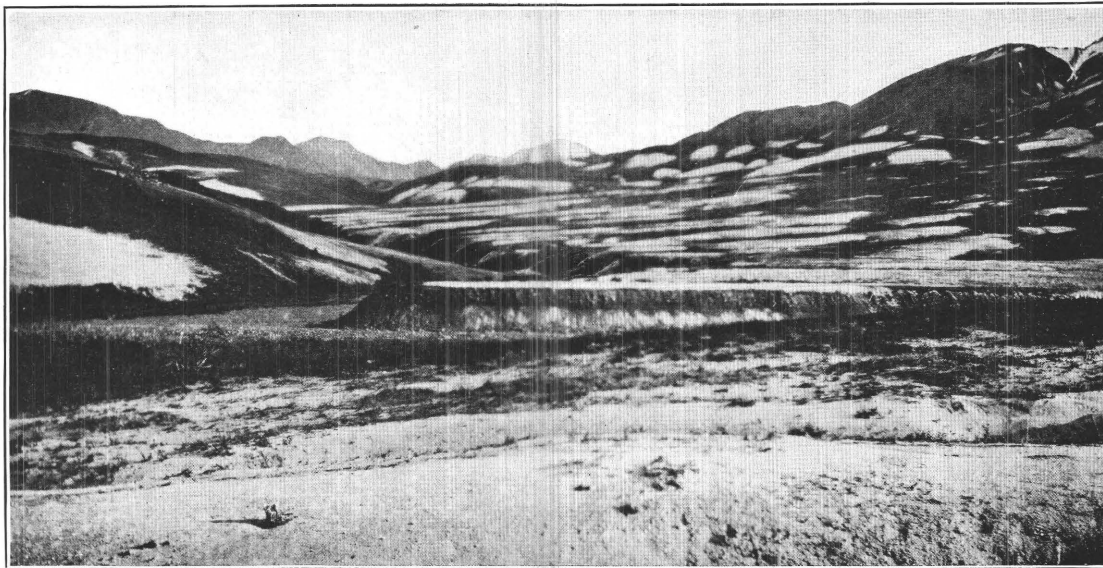


FIGURE 23.—Map of upper Yukon basin, Alaska and Yukon Territory, showing distribution of volcanic ash.

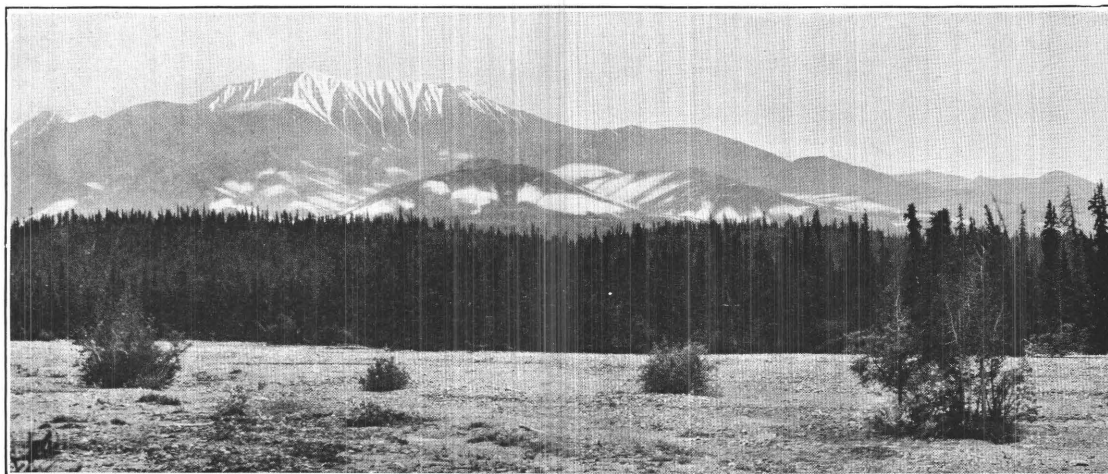
especially the spermphiles, or striped gophers, avail themselves of the ease with which the ash can be excavated, and their mounds are in many places composed almost entirely of this material. Furthermore, the low terraces of streams, covered with an ash layer, show that the material fell at a very late stage in the development of the present stream gravels. The ash overlies all but the most recent stream deposits and is much younger than the glacial materials deposited during the last great period of glaciation.

The thickness of the ash increases gradually, but by no means symmetrically, from the edges toward the center of the area covered. The great highway through this part of Yukon Territory and Alaska by way of the White Pass & Yukon route to the navigable waters of the Yukon basin follows directly across the ash-covered area, from southeast to northwest. Along this route the ash is particularly well exposed in the river banks. It first appears near Lake Bennett as a layer an inch or less in thickness, but increases to a maximum of about 1



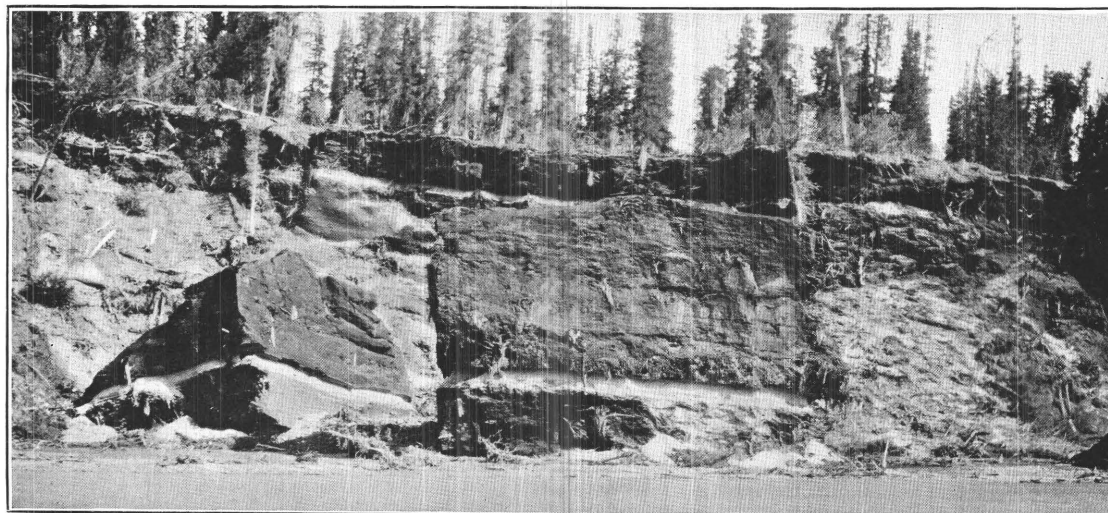
A. AN ASH-COVERED LANDSCAPE, UPPER KLETSAN CREEK, NORTHERN FOOTHILLS OF MOUNT NATAZHAT, ALASKA.

White deposit is ash except on high summits, which are covered with snow. Photograph by United States Coast and Geodetic Survey.



B. ASH DRIFT ON NORTHERN FOOTHILLS OF ST. ELIAS RANGE, ALASKA, NEAR INTERNATIONAL BOUNDARY.

Snow on high summits.



C. PEAT BLUFF, WITH VOLCANIC ASH LAYER, ON WHITE RIVER, ALASKA.

Overturnd peat blocks in foreground.

foot toward the northwest in a portion of the Teslin and Lewes river basins. Below Fort Selkirk it thins gradually northwestward, and beyond Eagle it is only an inch or less in thickness. Dawson¹ early recognized that the ash thickens from the Pelly westward toward the Lewes and must have come from the west. He suggests that it may have been derived from a volcano of the Mount Wrangell group. Hayes,² however, who crossed from Fort Selkirk to the head of White River in 1891, observed the increasing thickness of the ash to an area between Klutlan Glacier and Kletsan Creek, on the north flank of the St. Elias Range, and a rapid decrease in thickness west of that area. Brooks³ confirmed Hayes's observations in 1899. It was thus proved definitely that the material was not derived from the volcanoes of the Mount Wrangell group, but from some source much farther east. By a plotting of the observations obtained from all sources the data shown on figure 23 as to distribution and thickness of the ash were obtained. Within the area outlined by the 3-foot contour the ash occurs locally in great thickness. Hayes noted beds between 75 and 100 feet thick on the western bank of the Klutlan, where there is no reason to suppose that the original thickness had been increased at the expense of surrounding regions, except, perhaps, by wind drift. Near the head of Kletsan Creek, on both sides of the international boundary, there is an area 2 to 4 miles wide, along the mountain flank, in which the entire surface is covered with great white banks and dunes of ash (Pl. VI, A). The area is for the most part above timber line, vegetation on its surface is sparse or lacking, and from a little distance one receives the impression that he is looking over great banks of snow (Pl. VI, B). The surface of this area is dotted with lakelets, the ash shifts with the winds, and the hills are modified dunes. The presence of ground frost close to the surface, however, retards to some extent the movement of the ash by winds. The belt of thick ash has a relief of 200 to 400 feet, which is believed to be largely in the ash, as exposures of the underlying rocks are almost completely lacking.

It is quite evident from the great thickness of the ash along the south flank of the St. Elias Mountains near the international boundary that the vent from which it was ejected is in that neighborhood. Thomas Riggs, jr., while engaged in surveying the international boundary line, noticed a small crater in a glacial cirque 4 miles north-northeast of Mount Natazhat, from which he thinks it probable that the ash was ejected. The writer, in 1914, attempted to visit this crater, but a heavy snowfall early in July and a shortage of provisions prevented waiting until the snow should melt sufficiently to allow an inspection of the reported crater. All the evidence so far obtained, however, both as to the areal distribution of the ash and as to its thickness, points to some crater near the northern border of the St. Elias Mountains near the international boundary as the vent from which the ash came, and it is not improbable that the locality suggested by Riggs is the true one.

The distribution of the ash from its center of dispersion indicates that the winds at the time of the eruption blew from the west and south. The long east-west axis of the ash-covered area and particularly that of the area of ash 1 foot or more thick shows that the wind at the time of the greatest ash fall blew almost directly from west to east. The great breadth of the area in the north-south direction near its western margin also points to a shifting of the wind to the south, probably during the later stages of the eruption, for although ash was carried northward a distance of 300 miles from the crater, the 1-foot contour extends northward less than 50 miles from the center, whereas it reaches eastward a distance of at least 220 miles. The greatest distance from the center at which the ash layer has been recognized is on the eastern slope of the Mackenzie-Yukon Divide, in the basin of Gravel River, where J. Keele⁴ reports it, 450 miles from the center of dispersion. The southern limits of the ash area in the vicinity of the crater are not known, for they lie in an unexplored and almost inaccessible field of glaciers and rugged mountains. In figure 23, therefore, the southern margin is extended little beyond the area of thickest ash, though the ash may have fallen considerably farther south.

Estimates of the area covered by this ash deposit have been made from time to time, based on the facts as to distribution then available. The first of these estimates was made by Dawson,

¹ Op. cit., p. 44 B.² Op. cit., p. 148.³ Brooks, A. H., unpublished notes.⁴ Letter to A. H. Brooks.

in 1887. Although stating that the total area must necessarily be much greater than the area of his observations, he estimated a minimum area of 25,000 square miles covered by ash. Hayes, in 1891, with additional information at his disposal, increased the estimate to 52,280 square miles. Brooks, in 1906, after having extended the known distribution westward to longitude 143° W. and northward to the Yukon below Eagle, placed his estimate at about 90,000 square miles. By using some additional data, in particular Keele's observation of the ash in the basin of Gravel River, the writer has mapped (fig. 23) an area of 140,000 square miles covered by a layer of ash. It is well known that in volcanic eruptions of this kind, with extensive ejections of pumice, the dust remains in the air for a long time, and a film of ash, too thin to be observable after the lapse of centuries, is deposited over large areas of the earth's surface. No doubt if the facts were known, the area over which a visible layer of volcanic dust was deposited after this eruption would be measured as several hundred thousand or perhaps several millions of square miles.

Two estimates of the volume of ash ejected have been published. Dawson, assuming an area of 25,000 square miles and an average depth of ash of 3 inches, estimated that the ash would form a prism 1 mile square and 6,240 feet high. Hayes, taking an area of 52,280 square miles, assumed that the ash had the shape of a flat cone of that base, and an apex 50 feet in height. His estimate gave a volume of 165 cubic miles, over 138 times the figure reached by Dawson. It is obvious that this estimate is not based on defensible grounds, for the ash is not in the form of a cone, but if deposited on a level area its surface slopes would be decidedly concave. The distance from the head of Kletsan Creek north to White River is only about 12 miles, yet in that distance the ash decreases in thickness from 200 feet or more to less than 3 feet. According to Hayes's assumption, the ash should be 25 feet thick at distances of 110 to 185 miles from the center of dispersion. Observations over the area affected are still far too few to afford a basis on which accurate estimates of the amount of ash discharged can be made, but a provisional estimate, from the data now at hand, is given here. In making this estimate it has been assumed that in the outer zone, beyond the 1-foot ash contour, the ash averages 2 inches in thickness. This assumption seems reasonable, for over a large area of the outer zone average thicknesses of 5 to 6 inches have been observed, and even near the outermost margins a thickness of 1 to $1\frac{1}{2}$ inches is common. Between the 1 and 2 foot contours an average thickness of 15 inches is assumed, and between the 2 and 3 foot contours a thickness of 27 inches. The average thickness in the inner zone, with 3 feet or more of ash, is placed at 10 feet, although it is known that several hundred square miles is covered to depths of 25 to perhaps 300 feet or more with ash. The amount of ash derived by a calculation from the above figures gives a total volume of about 10 cubic miles. This figure is nearly eight and a half times that obtained by Dawson but only 6 per cent of that obtained by Hayes. The true figure is probably considerably more than 10 cubic miles, for no account has been taken of the great quantity of ash that fell as a thin film of dust far beyond the boundaries here shown.

The violence of the eruption at the time this ash was ejected may well be inferred by comparison with volcanic eruptions of historic times. Martin¹ has collected statistics on a number of such eruptions, and the figures used below are taken from his paper. The most violent volcanic eruption of historic record was that of Tomboro, on the island of Sumbawa, east of Java, in 1815. Estimates of the volume of material ejected reach figures of 26.6 to 50 cubic miles, and the area over which the ash fell was probably much greater than during the eruption here discussed. Krakatoa, in 1883, is said to have ejected an amount of ash about equal to that thrown out by Katmai, in June, 1912, or about 5 cubic miles. From the Katmai eruption the ash fall was perceptible at a distance of 1,200 to 1,500 miles. The greatest distance from the probable center of eruption in the White River basin to the margin of the ash fall, as now known, is only 450 miles, but it seems probable that if observations had been made at the time of the eruption, the distance would have been at least equal to that at which the Katmai ash was recognized. From the depth of the ash from the White River volcano at its thickest

¹ Martin, G. C., The recent eruption of Katmai Volcano, in Alaska: Nat. Geog. Mag., vol. 24, No. 2, 1913.

development, the area covered by it, and the enormous volume of material ejected, it is evident that the eruption was comparable in magnitude to any that have occurred during historic times. Unfortunately no facts are available, or are likely to be, as to the duration of the eruption, the violence of the detonations and the accompanying earthquakes, and the intensity and duration of the ash fall, which must have darkened the sun for days.

The physical and petrographic character of the ash at a number of places has been described by others, and no special study has been made by the writer. As was to be expected, the ash or pumice is coarsest near the center of eruption and becomes progressively finer as the distance from the center increases. Within the area of thickest ash the particles average perhaps from 1 to 3 millimeters in diameter, though larger pieces are numerous, and single fragments 8 or 10 centimeters in longest diameter were seen. Near the outer limits of the ash-covered area the material consists only of very fine dust. A sample collected by J. Keele from the basin of Gravel River, about 420 miles from the center of eruption, was subjected to a screening test and also measured under the microscope. The ordinary wire screens of 60, 80, 100, and 200 meshes to the inch were used, and the results are shown below, these sizes being reduced to millimeters:

Caught on 0.423-millimeter screen.....	per cent..	7.72
Caught on 0.317-millimeter screen.....	do....	2.46
Caught on 0.254-millimeter screen.....	do....	4.78
Caught on 0.127-millimeter screen.....	do....	11.28
Passed through 0.127-millimeter screen.....	do....	72.94

The material caught on the two coarsest screens contained a large proportion of vegetable matter and sand particles. As examined microscopically the largest particle of ash seen had a diameter of 0.25 millimeter; the smallest 0.002 millimeter; the average size appeared to be about 0.01 millimeter.

Dawson describes the ash from the Pelly and Lewes basins as—

a fine white sandy material, with a harsh feeling when rubbed between the fingers. Microscopically it is found to consist chiefly of volcanic glass, part being merely frothy and pumaceous, but of which the greater portion has been drawn out into elongated shreds, frequently resembling the substance known as Pele's hair, and in which the inclosed vesicles become more or less completely tubular. In addition to this glass, fragments and small perfect crystals of sanadine feldspar occur, together with portions of minute crystals of hornblende and probably other minerals.

Knopf,¹ who studied the coarser material from the White River basin in Alaska, gives the following description:

The "ash" is a white frothy glass, light enough to float on water. The larger fragments of the pumice inclose numerous small hexagonal plates of biotite, short prisms of hornblende a millimeter in length, and less conspicuous crystals of glassy feldspar. In thin section the hornblendes, which are deeply pleochroic in tones of brown, show ideally perfect cross sections and terminated prisms; the biotites are also finely developed and hold some inclusions of apatite. The feldspars are less perfectly crystallized. Both unstriated and lamellated varieties are present, but all possess indices notably higher than balsam. Zonal banding is not uncommon. Optical tests on striated Carlsbad twins prove that the feldspars belong to a species somewhat more calcic than Al_1An_1 . They inclose some minute foils of biotite. Grains of magnetite occur sporadically. The matrix holding these phenocrysts is a pumaceous glass, clear and colorless, with a marked drawn-out, twisted, and fluidal appearance. Some of the phenocrysts show that they were broken by the movements of the surrounding glass. According to the microscopical determination the ash is an andesitic pumice.

So far as is known, the ejection of the ash was unaccompanied by the outflow of lavas. No volcanic bombs or pyroclastic materials other than the ash have been noted, and it is probable that the outburst consisted solely of violent explosions which carried the ash outward but failed to yield other types of volcanic material.

All who have written of the volcanic ash in this district have recognized the fact that the eruption must have happened no great number of centuries ago. Dawson observed that as the rivers have not cut their beds perceptibly deeper since the deposit was laid down on their flood plains, the period to which the ash belongs can not be exceedingly remote. He also noted that at one place on the Lewes the ash rests upon a layer of stratified sands a few feet thick, and the

¹ Moffit, F. H., and Knopf, Adolph, op. cit., pp. 43-44.

sands overlie a mass of drift logs still quite sound and undecayed. From these and other facts Dawson believes that the date of the eruption, though at least several hundred years ago, can scarcely be more than a thousand years ago. Hayes arrives at a similar conclusion, but from different facts. He believes that the freedom of large ash areas from tundra moss, which covers with great readiness even the most barren surfaces, indicates the youth of the ash. He states that although great quantities of ash must have fallen on the surface of Klutlan Glacier and its névé fields, the fact that nearly all the ash now found there is in the terminal moraines, that on the stagnant ice extending only a short distance back from its front, indicates that since the eruption the ice which then formed the névé has moved the entire length of the glacier and deposited its ash in the terminal moraine. This he thinks must have required at least several hundred years. He also notes a retreat of the glacier front of about 3 miles since the ash fell.

During the summer of 1914 the writer made observations in White River basin that afford an opportunity for a more accurate calculation of the time that has elapsed since the ash fell. On White River, about 25 miles northwest of the supposed center of eruption, an excellent exposure shows a deposit of 39 feet of peaty vegetable material, interrupted 7 feet below its top by a 2-foot layer of ash (Pl. VI, C). The peculiar appearance of the roots of spruce trees growing on the surface of the peat suggested the possibility of determining the rate of peat accumulation at that place. The ordinary spruce tree of this region has a flat root base and sends its roots out radially, parallel with the surface. The roots penetrate only a few inches below the surface of the ground. In the locality just mentioned, however, each spruce tree has a central stem root, some of them several feet long, from which roots branch off at irregular intervals, including an upper set of roots near the surface, corresponding to those of the normal tree. The lower roots are in permanently frozen ground, and only the upper ones are functioning. It therefore seems evident that the trees as they grew were surrounded by a constantly thickening layer of vegetable material. In this material the level of ground frost rose as the deposit increased in thickness, the lower roots of the trees became permanently frozen, and the trees were forced to throw off adventitious roots near the surface repeatedly, in their efforts to survive. This study, details of which have been published elsewhere,¹ showed that dividing the age of a living tree, as indicated by the annual rings, by the thickness of the peaty deposit above the lowest roots gives a rate of accumulation of the peat of about 200 years to the foot. On that basis the volcanic eruption that caused the ejection of the widespread sheet of volcanic ash in the upper Yukon basin took place approximately 1,400 years ago.

Although perhaps the most recent volcanic eruption within the Yukon basin, the White River eruption offers by no means the only evidence of comparatively recent volcanic activity in that district, where lavas that were poured out subsequent to an earlier stage of Pleistocene glaciation are extensively developed. On the east branch of Dennison Fork of Fortymile River a volcanic crater, with associated lava flows, is so young that it still retains much of its original topographic form, and Quaternary lavas have been recognized elsewhere.

¹ Capps, S. R.: An estimate of the age of the last great glaciation in Alaska: Washington Acad. Sci. Jour., vol. 5, pp. 108-114, 1915.

EVAPORATION OF POTASH BRINES.

By W. B. HICKS.

INTRODUCTION.

It has long been known that many American brines, including ocean water, contain potassium along with much larger quantities of other salts, and during the last few years investigations have shown that brines from several different localities in the United States contain a high percentage of potassium. The development of an economic process for the extraction of potassium from these brines is a problem of great importance. The most practical methods so far proposed depend on evaporation and fractional crystallization. These facts suggest the desirability of knowing just what effect evaporation will have on the various constituents of a brine. Much is already known about the subject in a general way, and it is possible to predict certain qualitative relations concerning such simple salt solutions as those of sodium and potassium chlorides and also concerning solutions in general whenever the solid phases are known. Theoretically a saturated solution of sodium chloride containing a small amount of potassium chloride will deposit on evaporation only sodium chloride until the solution becomes saturated with respect to both salts; and a saturated solution of potassium chloride containing a small amount of sodium chloride will likewise deposit potassium chloride alone until equilibrium is reached. At 30° C. the saturated mixture¹ of these two salts contains 11.7 per cent of potassium chloride and 19.7 per cent of sodium chloride. On further evaporation at this temperature no change takes place in the composition of the solution, both salts being deposited in such quantities that the potassium-sodium ratios in both liquid and solid phases remain constant. Other instances of such simple relations could be given. Usually, however, solutions of two or more salts present much more complicated relations. The number of different ions present and the possible formation of other compounds, hydrates, and isomorphous mixtures are the chief factors influencing the complexity of the system. Consequently it is difficult to predict what changes will result through the evaporation of solutions containing several different ions. Furthermore, experiments with even the simplest systems do not yield the results that might be expected from a theoretical consideration. Precipitates often carry down mechanically or otherwise appreciable quantities of other salts, supersaturation may easily occur, and equilibrium is often slow in reaching its final adjustment. These are all factors of practical importance.

Experimental results relative to the changes which take place during evaporation, particularly with reference to potassium salts, are rather meager. In his evaporation studies on sea water Usiglio² found that the potassium in solution increased as evaporation proceeded, and the results of his experiments indicate in a general way what happens when sea water evaporates. However, in those early days the determination of potassium, and perhaps other constituents, was not capable of the refinement exacted in modern times. Usiglio found that the saline residue from sea water contained 0.71 per cent of potassium, while according to modern analyses³ the figure is about 1.1 per cent. Accordingly, it is assumed that Usiglio's determinations of potassium in the products of evaporation may have been likewise erroneous. Hence, it is not possible to calculate with any degree of assurance the amount of potassium which was lost by deposition from solution during evaporation. However, it appears that in

¹ Precht and Wittjen, *Deutsch. chem. Gesell. Ber.*, vol. 14, p. 1667, 1881.

² *Annales chim. phys.*, 3d ser., vol. 27, pp. 92, 172, 1849.

³ Clarke, F. W., *The data of geochemistry*, 2d ed.: U. S. Geol. Survey Bull. 491, p. 113, 1911.

concentrating the brine from 5 liters to about 100 cubic centimeters approximately 8 per cent of the potassium originally present was lost from solution. In the final mother liquor 3.31 per cent of the total salts was potassium, a condition which indicates that the potassium had still not saturated the solution, as the total salts of several sea water bitters from the vicinity of San Francisco are reported¹ to contain 5 to 10 per cent of potassium.

Chatard² evaporated large quantities of the water of Owens Lake, Cal., which, after being reduced to the point of crystallization contained about 0.8 per cent of potassium. The experiments were carried out at the normal temperature in the vicinity of Owens Lake. A series of crops of crystals were obtained, each of which contained about 1 per cent of potassium chloride. Unfortunately the weights of the salts and the mother liquors in each experiment are not reported, and consequently the relations can not be followed in detail. Another important factor, the analysis of the final mother liquor, is also lacking. However, it is probable that the solution did not become saturated with salts of potassium because each crop of crystals contained approximately the same percentage of this constituent. This conclusion is strengthened by similar results of the evaporation studies on the water of Mono Lake, Cal.² In the experiments at Mono Lake the final mother liquor was evaporated to dryness and the residue was analyzed. The potassium-sodium ratio in this product was 0.27, which is very strong evidence that the final mother liquor was not saturated with salts of potassium, experiments recorded elsewhere in the present paper having shown that in solutions very similar to that in Owens Lake the potassium-sodium ratio may become as high as 0.59. According to Chatard's results, about 15 per cent of the potassium originally present was lost in the evaporation water of Owens Lake long before the bittern became saturated with potash salts.

Evaporation studies on artificial potash brines were undertaken by the writer in the hope of throwing further light on the conditions governing the deposition of salts from solutions. It was planned to begin the investigation with simple salt mixtures and, by gradually including other salts, to deal finally with complex brines comparable with those found in nature. Though it has been possible to do only a small part of the experimental work contemplated, it seems advisable to publish the data thus far obtained, with the hope of supplementing them later.

In conducting the experiments an attempt was made to reproduce as far as possible commercial conditions. It is not believed that equilibrium reached final adjustment in the solutions, and consequently the results can not be considered as solubility determinations.

METHODS.

PREPARATION OF SOLUTIONS.

In the preparation of the solutions pure anhydrous chemicals were used except in the experiments with borates, for which borax was employed. The required amount of each salt was weighed out and dissolved in a definite volume of water. The composition of the original solutions as recorded in the tables was calculated from the data thus obtained.

METHOD OF EXPERIMENTATION.

In the preliminary experiments 150 grams of the solution under investigation was evaporated in a small beaker on the steam bath to about one-fourth its original volume and was allowed to cool at room temperature, which was between 25° and 30° C. The solution was stirred occasionally while cooling, and care was taken to start crystallization in order to prevent supersaturation. After the solution had cooled, it was filtered from the crystals by strong suction into a small flask, weighed, and analyzed.

In all other experiments 500 to 1,000 grams of solution was evaporated in beakers at intervals on the steam bath, and the progress of the results of evaporation was watched by removing from time to time the deposited salts and weighing and analyzing the solution. After each

¹ Phalen, W. C., The salt industry of the United States: U. S. Geol. Survey Bull. — (in preparation).

² Chatard, T. M., Natural soda: U. S. Geol. Survey Bull. 60, pp. 27-101, 1888.

stage in the evaporation the solution was stirred vigorously for several hours in an electrically controlled thermostat, which deviated less than 0.05° from 30° C., until the solution attained the temperature of the bath and appeared to be in equilibrium otherwise. It was then allowed to settle, and without change of temperature a sample of it was transferred by means of a pipette to a flask and weighed. The sample was drawn out through a filter consisting of a piece of cotton held in a small funnel which was attached to the pipette by a piece of rubber tubing. The pipette had a capacity of 8.606 cubic centimeters at 20° C., and from these data the specific gravity of the solution was calculated. The main portion of the solution was filtered into a smaller beaker with strong suction, as in the preliminary experiments, care being taken to remove as much as possible of the adhering liquid from the crystals. The filtrate was then returned to the steam bath and was further concentrated to about half its volume. It was then cooled in the thermostat, filtered from the crop of crystals, and otherwise treated as described above for the first product of evaporation, the filtrate being returned to the steam bath. The concentration was similarly continued at intervals until only a small amount of liquid remained. In all the experiments the procedure above described was followed in each succeeding stage in the evaporation.

METHODS OF ANALYSIS.

The weighed samples of solution obtained by the concentration just described were diluted to definite volume, and aliquot portions representing 3 to 4 grams of solution were taken for analysis. The determinations were made in duplicate, and practically all the figures given in the tables (pp. 68, 69, 71) are the average of two closely agreeing results. Common methods of analysis were usually employed, but short cuts were taken wherever possible, and a brief description of the procedure therefore seems advisable. The sulphate radicle was precipitated and weighed as barium sulphate, and potassium was estimated by the modified chlorplatinate method.¹ Sodium was determined by weighing the combined bases as chlorides or as sulphates and subtracting the corresponding equivalent of the potassium, borates when present being first removed by repeated evaporation with methyl alcohol and hydrochloric acid. Chlorine was determined by titration with N/10 silver nitrate after neutralizing the solution with nitric acid. The borate radicle was estimated by titration of the boric acid with N/10 sodium hydroxide in the presence of mannite and phenolphthalein. The carbonate radicle was determined by titrating with N/10 hydrochloric acid in the presence of methyl orange and subtracting the borate equivalent.

The calculations were made with the slide rule, and a few of the results may differ slightly from the true amounts. The percentage of the various constituents lost during evaporation is stated in round numbers with two significant figures, and no correction was made for the amount of salts removed with the sample for analysis.

¹ Hicks, W. B., A rapid modified chlorplatinate method for the estimation of potassium: Jour. Ind. Eng. Chem., vol. 5, pp. 650-653, 1913.

EXPERIMENTAL RESULTS.

PRELIMINARY EXPERIMENTS.

In the preliminary experiments solutions nearly saturated with salts of sodium and containing much smaller amounts of salts of potassium were concentrated on the steam bath to about one-sixth their original volume, it being assumed that the resulting solutions would be approximately saturated with potash salts. The solutions were cooled at room temperature, filtered, and analyzed. The results are given in the following table, together with the composition of the original solution and other data:

Changes resulting from the evaporation of artificial potash brines containing one acid radicle.

Character of solution.	Solution before evaporation.			Solution after evaporation.					Potassium lost (per cent).	K/Na ratios.		
	Quantity (grams).	Sodium (grams).	Potassium (grams).	Quantity.		Sodium (per cent).	Potassium.					
				Grams.	Per cent.		Per cent.	Grams.				
KCl+NaCl.....	150	5.901	1.573	24.1	16	8.50	4.58	1.104	30	0.27	0.54	a.79
K ₂ CO ₃ +Na ₂ CO ₃	150	4.882	1.698	21.3	14	9.36	6.22	1.326	22	.35	.67
K ₂ SO ₄ +Na ₂ SO ₄	25	.737	.225	6.3	25	4.72	2.72	.170	24	.31	.58

^a Precht and Wittjen, Deutsch. chem. Gesell. Ber., vol. 14, p. 1667, 1881.

According to these results, the potassium appears to have concentrated most rapidly in the carbonate and least rapidly in the sulphate solution, and the potassium-sodium ratio after evaporation is greatest in the carbonate solution. It is apparent from the column of ratios that the chloride solution had not become saturated with potassium, and it is probable that the other concentrated brines had not reached equilibrium. The loss of 20 to 30 per cent of the potassium during evaporation shows that a large part of the potassium is removed from such brines before the solution becomes saturated with this constituent.

ALKALI BRINES CONTAINING TWO ACID RADICLES.

In the evaporation experiments with brines containing two acid radicles the original solutions were approximately of the same strength and contained three to four times as much sodium as potassium. In each series of experiments 500 grams of the solution was evaporated in stages, and the effect of each partial concentration was determined by analyzing the solution according to the methods already described. The character of the brines, their original composition, and the results of evaporation are given in the accompanying table. The changes in the concentration and the percentage loss of potassium as evaporation proceeded are also shown graphically in figures 24 and 25 (p. 70).

Changes resulting from the evaporation of artificial potash brines containing two acid radicles.

Character of solution.	Stages in the evaporation. ^a	Solution after evaporation.		Specific gravity.	Percentage composition of the solution.					Percentage loss.				K/Na ratio.
		Grams.	Per cent.		K.	Na.	Cl.	CO ₃ .	Total salts.	K.	Na.	Cl.	CO ₃ .	
KCl+Na ₂ CO ₃	A	500	100.0	2.10	6.94	1.90	9.06	20.00	0.30
	1	236	57.2	1.35	4.09	11.51	3.68	15.05	34.33	8.0	22	8.5	22	.36
	2	141	28.2	1.36	5.67	10.97	5.14	14.44	36.22	24	55	24	55	.52
K ₂ SO ₄ +Na ₂ CO ₃	3	49	9.8	1.36	7.48	10.03	6.71	13.28	37.50	65	86	65	86	.73
	A	500	100.0	1.80	6.94	2.20	9.06	20.00	SO ₄26
	1	192	38.4	1.39	3.06	13.00	3.12	17.33	36.51	35	28	46	27	.24
KCl+NaCl+Na ₂ SO ₄ ...	2	58	11.6	1.38	3.68	12.30	2.56	17.17	35.71	76	79	87	78	.30
	A	500	100.0	2.10	6.87	11.61	1.19	21.77	Cl	SO ₄	.31
	1	249	49.8	1.24	3.99	9.16	16.16	2.26	31.57	5.3	34	27	5.4	.44
KCl+NaCl+NaCO ₃ ...	2	128	25.6	1.25	5.55	8.54	16.72	1.96	32.77	32	68	63	58	.65
	3	41	8.2	1.26	6.24	8.22	17.18	1.56	33.20	76	90	88	89	.76
	A	500	100.0	2.10	8.03	11.61	2.26	24.00	CO ₃26
KCl+NaCl+NaCO ₃ ...	1	277	55.4	1.26	3.55	10.06	14.72	3.43	31.76	6.4	31	30	16	.35
	2	117	23.4	1.29	5.51	9.77	14.02	5.18	34.48	39	72	72	46	.56
	3	60	12.0	5.39	10.50	12.30	7.47	35.66	69	84	87	60	.51
KCl+NaCl+Na ₂ B ₄ O ₇ ..	4	40	8.0	5.10	11.12	11.22	8.98	36.42	81	89	92	68	.46
	A	500	100.0	2.10	(?)	11.61	B ₄ O ₇ (?)	B ₄ O ₇
	1	166	33.2	5.14	8.38	17.29	1.08	31.89	19	(?)	51	(?)	.61
KCl+NaCl+Na ₂ B ₄ O ₇ ..	2	95	19.0	6.21	8.00	17.41	1.60	33.22	44	7178
	3	38	7.6	6.11	8.15	17.10	2.28	33.64	78	8975

^a A=original solution.

The highest concentration of potassium, 7.48 per cent, was obtained with the solution containing potassium chloride and sodium carbonate and the lowest, 3.68 per cent, with that containing potassium sulphate and sodium carbonate. In the chloride-sulphate and chloride-borate brines the concentration of potassium increased to a little more than 6 per cent, but in the solution containing potassium chloride, sodium chloride, and sodium carbonate it increased to a maximum and then decreased. In general the contents of sulphate and sodium varied comparatively little after the first concentration. The chlorine concentration usually increased as evaporation progressed, but in the solution containing potassium chloride, sodium chloride, and sodium carbonate it decreased after the first concentration. In that solution the content of carbonate continually increased, but in the other carbonate brines it rapidly rose to a maximum and then slowly declined. The final mother liquor always contained a large amount of carbonate. The borate concentration steadily increased. The amount of dissolved salts increased in all the solutions to more than 33 per cent. The two solutions containing both chloride and carbonate yielded the strongest bitters. The variations in the potassium-sodium ratio correspond closely to the changes in the concentration of the potassium. The highest ratio was reached in the chloride-borate solution, and the lowest in the sulphate-carbonate solution. The loss of potassium during the first concentrations was greatest in the sulphate-carbonate solution. The loss of potassium during the first concentrations was greatest in the sulphate-carbonate brine. In all the other solutions the loss was only 5 to 8 per cent while the solution was being concentrated to about half its original volume and the content of potassium was being doubled. During further evaporation the loss was very rapid in all the solutions. The steady increase in the percentage of total salts and the continual variations in the concentration of the constituents prove that equilibrium in the solutions did not reach final adjustment.

The variations in concentration of the potassium in the several solutions as evaporation proceeded are shown graphically in figure 24. The curve representing the solution containing

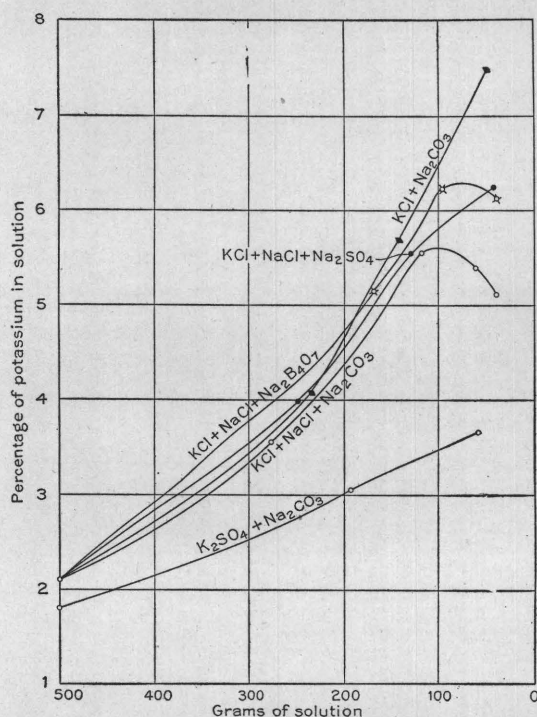


FIGURE 24.—Diagram showing the rate of concentration of potassium in various brines during evaporation.

in that containing potassium sulphate and sodium carbonate. With the exception of the curve for the latter solution the curves are all very much alike, sloping gently to a point corresponding to about half the quantity of the original solution and then becoming very steep. In other words, the loss of potassium sustained by the solutions during reduction to half their original volume and during concentration of the potassium to about 4 per cent is 5 to 8 per cent of that originally present, but during further evaporation the loss is very rapid.

ALKALI BRINES CONTAINING THREE ACID RADICLES.

More extensive evaporation experiments were carried out with solutions of the alkalis containing sulphate or borate in addition to chloride and carbonate. The character and composition of the brines used and the changes resulting through evaporation are given in the accompanying table. The change in concentration and the percentage loss of potassium for the sulphate solution is plotted in fig. 26 (p. 72).

The corresponding curves for the borate solution are so nearly identical with those given that they would unnecessarily confuse the diagram.

The curve representing the solution containing potassium sulphate and sodium carbonate is practically a straight line whose moderate slope indicates that the concentration of the potassium is slow and the loss of it necessarily large. The curves representing the concentration of potassium in the other solutions are similar to one another up to a concentration of about 5.5 per cent; beyond that point the curve for the solution of potassium chloride, sodium chloride, and sodium carbonate declines immediately and that of the borate reaches a maximum at 6.21 per cent.

Figure 25 gives a better idea of the losses of potassium sustained by the solutions than the table. From this it appears that at any particular stage in the evaporation the loss was least in the solution containing potassium chloride and sodium carbonate and greatest

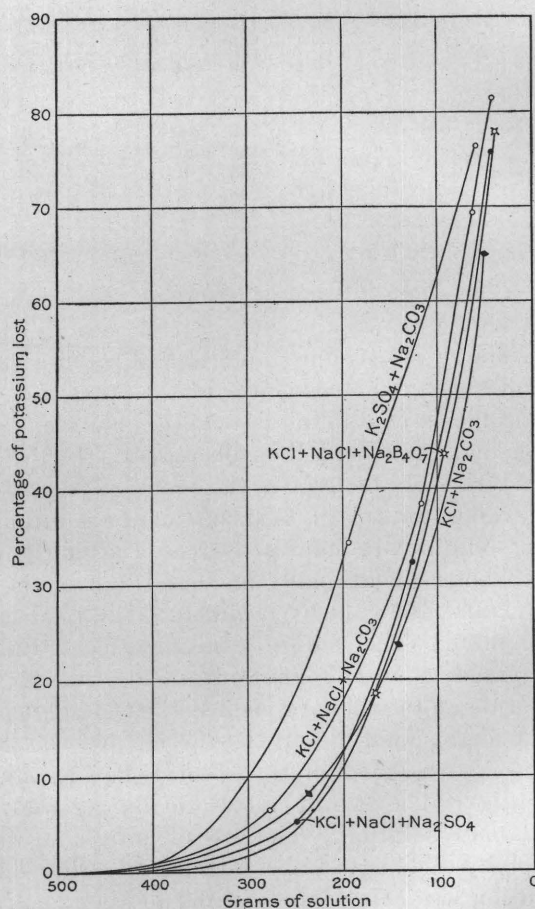


FIGURE 25.—Diagram showing the loss of potassium in various brines during evaporation.

Changes resulting from the evaporation of artificial potash brines containing three acid radicles.

Character of the solution.	Stages in the evaporation. ^a	Solution after evaporation (grams).	Specific gravity.	Percentage composition of the solution.						Potassium in total salts (per cent).	Percentage loss.					K/Na ratio.
				K.	Na.	Cl.	CO ₃ .	SO ₄ .	Total salts.		K.	Na.	Cl.	CO ₃ .	SO ₄ .	
KCl+NaCl+Na ₂ CO ₃ +Na ₂ SO ₄ ..	A	1,000	1.223	2.10	9.18	11.60	2.26	2.39	27.53	7.63	0.23
	1	723	1.268	2.86	10.64	13.53	2.68	3.05	32.76	8.73	1.6	16	16	14	7.5	.27
	2	547	1.278	3.67	10.40	13.51	3.16	2.96	33.70	10.89	4.4	38	36	24	32	.35
	3	337	1.285	4.88	9.82	13.71	3.63	2.30	34.34	14.20	22	64	60	46	67	.50
	4	213	1.295	5.75	9.79	13.39	4.79	1.79	35.51	16.19	42	77	75	55	84	.59
	5	148	1.300	5.70	9.93	13.20	5.08	1.67	35.58	16.02	60	84	83	67	90	.57
	6	99	1.314	5.53	10.33	12.18	6.51	1.55	36.10	15.31	74	89	89	71	93	.54
	7	55	1.327	5.34	11.01	11.24	7.84	1.56	36.99	14.44	86	93	95	81	96	.49
	8	22	1.335	5.28	11.26	10.86	8.36	1.59	37.35	14.14	94	97	98	92	98	.47
KCl+NaCl+Na ₂ CO ₃ +Na ₂ B ₄ O ₇ ..	A	1,000	1.238	2.10	(?)	11.60	2.27	B ₄ O ₇ (?)
	1	653	1.260	3.13	10.18	14.37	3.05	1.46	32.19	9.72	2.6	19	1231
	2	541	1.270	3.57	10.25	14.10	3.57	1.70	33.19	10.76	8	34	1535
	3	355	1.284	4.65	9.86	13.80	3.88	2.18	34.37	13.53	23	58	3947
	4	248	1.310	5.60	9.74	13.23	4.67	3.01	36.25	15.45	34	72	4957
	5	165	1.339	5.26	10.53	11.82	6.23	4.13	37.97	13.85	59	83	5550
	6	104	1.368	5.11	11.10	10.90	7.02	5.45	39.58	12.91	75	90	6846
	7	49	1.378	5.03	11.45	9.46	8.77	6.29	41.00	12.27	88	96	8144
	8	17	1.388	4.82	11.80	9.42	8.63	6.39	41.06	11.74	96	98	9341

^a A—original solution.

As evaporation progressed the potassium concentration of both solutions increased to about 6 per cent and then gradually decreased. The chlorine concentration rose to a maximum in each solution and then decreased. The carbonate concentrates increased rapidly in both brines, but finally showed a slight decrease in the borate solution. The borate concentration rose steadily to 6.39 per cent. The changes in the percentages of sulphate and sodium were slight. The quantity of dissolved salts in both solutions became greater as evaporation progressed. The final sulphate mother liquor contained 37.35 per cent of salts and that of the borate 41.06 per cent.

In the sulphate solution the potassium-sodium ratio increased from 0.23 to 0.59 and then decreased to 0.47. In the borate solution it reached a maximum of 0.57 and then decreased to 0.41.

The percentage of potassium lost from both solutions increased slowly until the brines had been reduced to about half their original volume. At this point the concentration of the potassium was about 4 per cent, and the loss amounted to 5 or 6 per cent of the potassium originally present. On further evaporation the loss was very rapid. At the maximum concentration of potassium only about one-fifth of the solution remained, and a loss of more than 35 per cent is recorded. By means of the curves in figure 26 the percentage loss corresponding to any concentration of potassium can be directly determined.

CONCLUSION.

According to the results set forth in this paper, the potassium is concentrated best in brines containing carbonates and chlorides, and poorest in those containing sulphates and carbonates, though a small amount of sulphate does not seem to hinder the concentration materially. In brines that contain several acid radicles the concentration of potassium may increase to a maximum as evaporation proceeds and then decline. The evidence at hand indicates that a large percentage of the potassium in a solution is lost during evaporation before the maximum con-

centration of potassium is attained. The loss is small until the potassium reaches a concentration of about 4 per cent, but it is very rapid during further evaporation. Therefore in the commercial extraction of potash from brines, especially those of the alkalis, it would seem

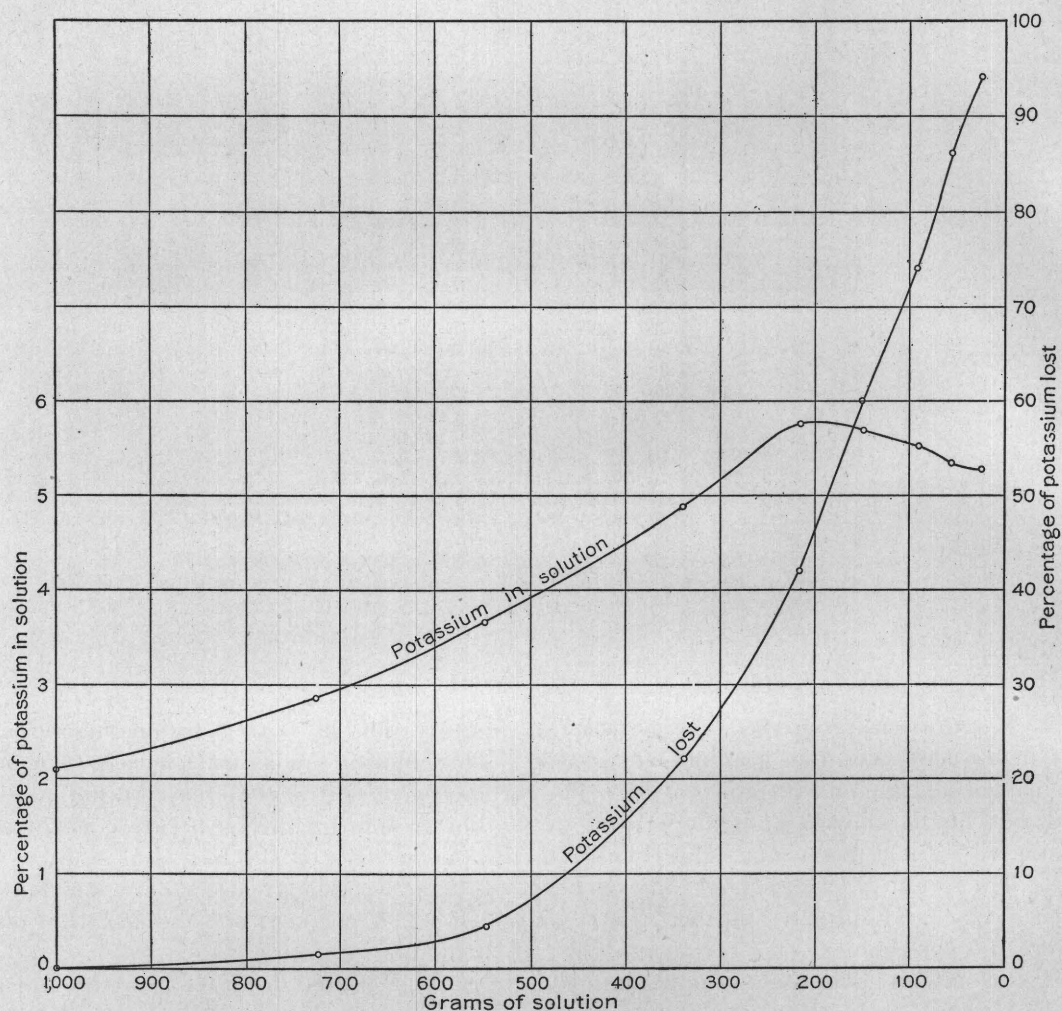


FIGURE 26.—Diagram showing the rate of concentration and the loss of potassium during the evaporation of a brine containing chlorides, carbonates, and sulphates of the alkalis.

best first to concentrate the solution by evaporation until it contained about 4 per cent of potassium, and then to subject the resulting bittern to other processes of manufacture. The most advantageous point of concentration would, however, have to be determined for each particular brine.