

IMPERIAL INSTITUTE

MONOGRAPHS ON MINERAL RESOURCES
WITH SPECIAL REFERENCE TO THE
BRITISH EMPIRE

PREPARED UNDER THE DIRECTION OF THE
MINERAL RESOURCES COMMITTEE OF THE
IMPERIAL INSTITUTE WITH THE ASSISTANCE
OF THE SCIENTIFIC AND TECHNICAL STAFF

POTASH

NEW EDITION, REVISED AND ENLARGED, BY
SYDNEY J. JOHNSTONE, B.Sc. (LOND.), A.I.C.
SCIENTIFIC AND TECHNICAL DEPARTMENT, IMPERIAL INSTITUTE

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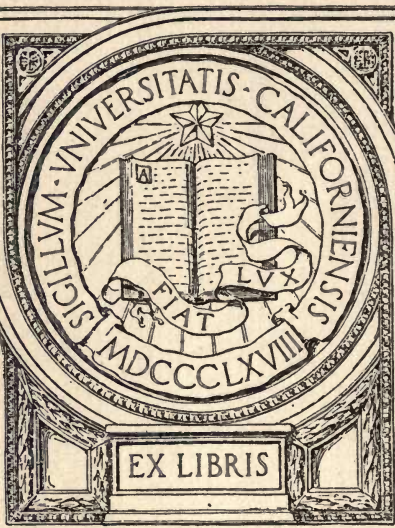
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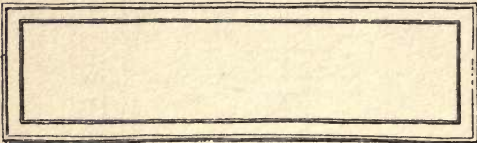
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THE Imperial Institute is a centre for the exhibition and investigation of minerals with a view to their commercial development, and for the supply of information respecting the sources, composition, and value of minerals of all kinds.

The Imperial Institute is provided with Research Laboratories for the investigation, analysis, and assay of minerals, and undertakes reports on the composition and value of minerals, for the information of Governments and producing companies and firms, in communication with the principal users in the United Kingdom and elsewhere in the Empire.

Important minerals from within the Empire are exhibited in the respective Courts of the Public Exhibition Galleries, and also in the Mineral Reference Collections of the Institute.

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GENERAL PREFACE

THE Mineral Resources Committee of the Imperial Institute has arranged for the issue of this series of Monographs on Mineral Resources in amplification and extension of those which have appeared in the *Bulletin of the Imperial Institute* during the past fifteen years.

The Monographs are prepared either by members of the Scientific and Technical Staff of the Imperial Institute, or by external contributors, to whom have been available the statistical and other special information relating to mineral resources collected and arranged at the Imperial Institute.

The object of these Monographs is to give a general account of the occurrences and commercial utilization of the more important minerals, particularly in the British Empire. No attempt has been made to give details of mining or metallurgical processes.

HARCOURT,
Chairman, Mineral Resources Committee.

Imperial Institute, London, S.W.7
July 1920.

CONTENTS

CHAPTER I

INTRODUCTION

	PAGE
<i>United Kingdom Imports and Exports of Potash ; World and United States Outputs of Potash</i>	I

CHAPTER II

DEPOSITS OF SOLUBLE POTASH MINERALS

<i>Germany ; France ; Holland ; Denmark ; Poland ; Russia ; Spain ; India ; Canada ; Abyssinia ; Nigeria ; Peru</i>	7
---	---

CHAPTER III

SALT LAKES AND PANS

<i>United States ; India ; China ; Tunis ; Morocco ; Chile ; Canada</i>	26
---	----

CHAPTER IV

POTASSIUM NITRATE DEPOSITS OF MINERAL ORIGIN

<i>Chile ; Rhodesia ; Russia ; Brazil ; Venezuela</i>	37
---	----

CHAPTER V

POTASSIUM NITRATE DEPOSITS OF ORGANIC ORIGIN

<i>India ; Mexico ; Guatemala ; Peru ; United States ; Rhodesia ; Union of South Africa ; Upper Egypt</i>	40
---	----

CHAPTER VI

SEA WATER AS A SOURCE OF POTASHPAGE
49

CHAPTER VII

INSOLUBLE POTASH MINERALS

ALUNITE: <i>Composition of Alunite; Extraction of Potash from Alunite</i>	51
FELSPARS AND OTHER SILICATES: <i>Extraction of Potash from Felspars, etc.</i>	60
INSOLUBLE POTASH MINERALS AS FERTILIZERS	69

CHAPTER VIII

FLUE GASES AS SOURCES OF POTASH

CEMENT KILN DUST	72
BLAST FURNACE DUST	80

CHAPTER IX

VEGETABLE SOURCES OF POTASH

MARINE PLANTS: <i>Scotland; Ireland; Norway; Japan; South Africa; Canada; United States</i>	87
RAW SEAWEED AS A POTASH FERTILIZER	96
WOOD ASH	97
VEGETABLE WASTE: <i>Hedge Clippings; Sunflower Stalks; Water Hyacinth; Bracken</i>	102
OTHER VEGETABLE SOURCES OF POTASH	106

CHAPTER X

RESIDUES FROM BEET-SUGAR MANUFACTURE 107

CHAPTER XI

ANIMAL SOURCES OF POTASH

WOOL WASHINGS	110
KARROO ASH	112

REFERENCES TO LITERATURE ON POTASH 114

NOTE.—Numerals in square brackets in the text refer to the Bibliography at the end.

POTASH

CHAPTER I

INTRODUCTION

MOST of the potash used throughout the world has, for many years past, been supplied from the deposits at Stassfurt, in Germany. Owing to the favourable situation and magnitude of these deposits, almost all other sources have proved, in comparison, unremunerative to work.

At the outbreak of the war the greater part of the world was confronted with a scarcity of potash salts, and efforts were made to revive old sources previously considered unworkable on account of cost, and also to discover possible new sources.

The importance of an adequate supply of potash for agricultural purposes is well shown by the following table which gives the consumption of potash (K_2O), in metric tons, in the more important countries during the four years preceding the war [1/p. 292].

—	England.	France.	United States.	Germany.
1910 . . .	18,258	22,849	244,910	359,335
1911 . . .	20,902	26,468	237,442	422,340
1912 . . .	23,414	31,691	215,965	463,383
1913 . . .	23,410	33,115	231,689	536,102

It has been calculated that the following quantities of potash (K_2O), per square kilometre, were applied as fertilizer to land during 1912: in Germany, 1.400; England, 0.183; United States, 0.129; France, 0.096 metric tons, respectively. During the war the consumption of potash fertilizers in Germany increased considerably, the amounts used during 1916 and 1917 being equivalent to 681,000 and over 800,000 metric tons of potash (K_2O) respectively, as compared with 536,102 tons in 1913.

In the present monograph most of the old and the new sources are described so far as details are available. Certain of these will probably only be utilized so long as the price of potash is high, but others, such as those of Alsace, have already become competitors with the Stassfurt deposits.

The values of potash salts imported into and exported from the United Kingdom during the past few years have been as shown in the accompanying tables (pp. 3-4) [2].

The sources of potash may be roughly classified into (1) solid deposits of soluble potash minerals, such as carnallite, sylvite and kainite; (2) sea-water, brines and salt-lake deposits containing appreciable amounts of potash salts associated with sodium salts; (3) vegetable substances, such as wood ashes, beet-sugar residues, seaweed and sunflower stalks; (4) animal material, such as wool washings; (5) products resulting from the decay of organic nitrogenous matter, such as Indian nitre; (6) dust carried in flue gases from the manufacture of cement and iron; (7) insoluble potash minerals, such as alunite, felspar, leucite, etc. Each of these sources will be considered in detail.

Complete statistics of the quantity of potash produced recently from all sources are not available, but the details concerning the outputs from the United States, in short tons, are of interest (*see* p. 6) [4] [24] [85] [176] [177]. These show that if the production during 1916, which was 9,720 tons, be taken as unity, then the outputs of succeeding years will be represented by 3.35, 5.61, 3.34 and 4.94 respectively. The production during 1918 amounted to about 22 per cent. of the normal consumption of the United States.

Potash Salts Imported into the United Kingdom

	1912.	1913.	1914.	1915.	1916.	1917.	1918.	1919.
<i>Potassium nitrate :</i>								
Germany	143,613	156,682	92,058	—	160	—	—	—
Netherlands	1,209	271	1,563	—	—	—	—	—
Belgium	25,273	25,023	19,270	—	—	—	—	—
United States	—	—	3,258	18,817	—	—	—	—
Other foreign countries	2,851	2,359	4,457	294	—	1,838	—	—
British India	44,244	56,631	109,145	363,830	807,579	839,191	835,921	276,906
Other British Possessions	—	—	484	25	—	—	—	—
Total	217,190	240,966	230,244	382,966	807,739	841,029	835,921	276,906
<i>Other potash salts :</i>								
Russia	83,921	58,499	28,729	40,245	262,226	40,728	98,310	106,025
Sweden	9,060	12,634	25,642	24,297	17,842	—	350	12,995
Germany	420,903	441,436	237,986	26,014	232	—	1,463	125,102
Netherlands	790	769	34,776	37,118	—	—	2,770	165,288
Belgium	23,719	20,489	17,929	5	—	—	—	482
France	54,297	57,115	48,958	88,179	42,378	31,553	52,118	54,693
Japan	16,730	30,654	28,790	32,587	65,428	66,335	84,967	58,239
United States	3,921	2,946	28,084	141,772	162,220	139,228	37,920	67,420
Other foreign countries	736	1,292	35,998	78,446	49,679	26,177	23,418	23,421
Total from foreign countries	614,077	625,834	486,892	468,663	600,005	304,021	301,316	613,665
Total from British Empire	5,084	4,400	4,509	24,963	35,025	25,134	148,741	20,296
Total	619,161	630,234	491,401	493,626	635,030	329,155	450,057	633,961

POTASH

Exports of Potassium Compounds from the United Kingdom

	1913.	1914.	1915.	1916.	1917.	1918.	1919.
<i>Manufactured in the United Kingdom :</i>							
Saltpetre	£ 46,580	£ 30,048	£ 43,593	£ 48,686	£ 30,636	£ 53,286	£ 151,023
Chromate and bichromate of potash	81,456	52,762	26,396	33,638	63,256	48,109	107,390
Other sorts	130,960	114,986	133,571	84,342	54,393	32,923	89,715
<i>Foreign and Colonial Merchandise :</i>							
Saltpetre	9,815	7,869	89,262	204,116	138,277	124,075	63,538
Other sorts	71,948	33,790	52,408	49,409	22,516	31,733	45,570

World's Production of Potash, 1913-1920
(Metric tons)

Source.	Nature of Products.	Estimated percentage of Potash (K ₂ O).	1913.	1914.	1915.	1916.	1917.	1918.	1919.	1920.
Abyssinia	Potassium chloride .	About 50	nil	nil	nil	2,500	3,578	— *	934	1,087
Australia ⁶	Alunite	6 to 9.5	2,271	3,109	1,443	477	1,846	3,461	2,586	664
Canada ^{6,2}	Pot and Pearl ashes	30 to 56	550	434	453	481	135	180	135	— *
Chile	Crude potassium nitrate	About 12	nil	nil	— *	— *	— *	— *	— *	— *
France ⁵	Kainite (<i>see p. 12</i>)	15 to 20	355,341	325,886	114,358	204,474	320,131	333,499	500,000	1,110,000
Germany ^{1,6}	<i>See p. 10</i>	100	1,110,274	904,137	679,975	883,606	1,004,282	1,001,364	812,002	924,168
Br. India ⁶	Saltpetre	About 40	15,326	16,064	18,708	20,083	22,537	25,922	17,832	— *
	Potash salts	—	—	—	—	—	—	—	84	— *
Italy ⁶	Alunite	7 to 73	5,976	3,700	4,850	3,370	2,455	2,017	3,307	— *
Japan	Kelp ash	17 to 24	—	—	—	—	—	—	—	— *
Norway ³	Kelp ash	17 to 24	— *	— *	535	797	1,809	559	— *	— *
Poland ⁶	<i>See p. 15</i>	10	17,200	— *	— *	— *	— *	— *	— *	5,000
Russia ³	Potassium carbonate from sunflower stalk ash	60	6,953	— *	— *	— *	— *	— *	— *	— *
Sweden	Kaikalk	5-6	— *	— *	— *	— *	— *	— *	— *	— *
Tunis	Seb-kainite	100	nil	nil	nil	nil	(733 =	— *	— *	— *
United Kingdom ⁶	Kelp ash ⁴	17 to 24	7,113	6,930	6,517	4,217 ⁷	2,531 ⁷	3,635 ⁷	— *	— *
								1,200 ⁸		
United States ⁶	<i>See p. 6</i>	100	— *	— *	989	8,820	29,558	49,717	29,460	43,615

¹ Sales.

² Barrels exported.

³ Exported.

⁴ Not including raw seaweed used directly as a manure. Figures are for Scotland and Ireland.

⁵ De Retz "Rapport," Alsace Trading Co. [191].

⁶ Official figures. ⁷ Exports from Ireland. ⁸ Consumed in Ireland.

* Figures unpublished or unobtainable.

Outputs of Potash in the United States

Source.	Content of available potash (K ₂ O).			
	1917.	1918.	1919.	1920.
Natural brines and Salt Lakes	20,652	39,716	21,590	37,515
Alunite	2,402	2,621	2,294	2,076
Cement kiln dust	1,621	1,549	1,258	1,147
Blast furnace dust	185	205	94	173
Seaweed	3,572	4,804	132	205
Molasses residues from distilleries	2,846	3,467	2,892	3,253
Wood ashes	621	673	484	263
Sugar refining waste	369	1,374	3,601	3,394
Silicate rocks	—	105	127	51
Miscellaneous sources	305	289	2	—
	32,573	54,803	32,474	48,077

The potash producing capacity of the United States is about 100,000 tons per year from the following sources :

Nebraska and other brine lakes	78,000
Alunite	4,000
Dust from cement mills	3,500
Kelp	5,500
Molasses and sugar-refining waste	7,000
Wood ashes	1,000
Other sources	1,000

The average price per unit for potash salts produced in the United States has fallen considerably since 1916, as shown by the following :

	1915.	1916.	1917.	1918.	1919.	1920.
Price \$	3.14	4.37	4.29	4.11	2.31	1.80

CHAPTER II

DEPOSITS OF SOLUBLE POTASH MINERALS

Germany.—The most important deposits of this type hitherto worked on an extensive scale are the Stassfurt deposits of Germany, which are of Permian age.

It is not intended to give in this monograph a complete account of these deposits, but a brief outline is necessary in order to convey an adequate idea of their general relationship to other sources, and particularly to deposits recently located elsewhere. The Stassfurt deposits had been worked near the surface for salt since the thirteenth century, but their value as a source of potash was only discovered about 1857, when shafts were being sunk in search of further deposits of rock salt. In 1861 the regular production of potash salts commenced, and has continued in increasing volume ever since. Exploration has shown that the deposits cover an area of 100 square miles, extending to Thuringia on the south, Hanover on the west, and Mecklenburg on the north. It has been estimated that these deposits occupy a volume of 10,790 million cubic metres, containing 20,000 million metric tons of potash salts, a quantity sufficient to supply the world for 2,000 years at the present rate of consumption. The deposits vary considerably from point to point, but the following may be taken as representing an average sequence. Starting from the surface, there occurs about 26 ft. of drift, followed by shales, sandstones and clays of varying thicknesses. The saline deposits often start here with a varied thickness of rock salt, which is followed by 98 to 262 ft. of *anhydrite* (anhydrous calcium sulphate, CaSO_4), 16 to 33 ft. of salt clay and 49 to 131 ft. of *carnallite* (double chloride of magnesium and potassium, $\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$). In certain parts of the field this is succeeded by varying thicknesses of *kainite* (KCl ,

MgSO₄.3H₂O) mixed with *sylvite* (potassium chloride, KCl), rock salt, and *picromerite* (sulphate of potassium and magnesium, K₂SO₄.MgSO₄.6H₂O). Then occur deposits of *kieserite* (magnesium sulphate, MgSO₄.H₂O), *polyhalite* (sulphate of calcium, potassium and magnesium, 2CaSO₄.K₂SO₄.MgSO₄.2H₂O), rock salt and *anhydrite*, somewhat interbedded, the total thickness varying from 490 to 3,280 ft. Finally, beds of *anhydrite* and *gypsum* are found. In all, over thirty minerals, mostly double salts, have been found in these deposits. Economically the most important are *carnallite* and *kainite*.

Space will not permit of a description of the methods of working these deposits, but it may be mentioned that in 1913 the cost of production of the various salts was stated to be as follows: Kainite, 7s. 2d.; potassium chloride, 61s. 10d.; potassium sulphate, 89s. 1d.; fertilizer salt, 42s. per ton. Since 1915 these costs have been considerably increased by the rise in wages and the cost of stores (*see* p. 9).

The mines are controlled by the Potash Syndicate (Kali-syndikat), which was first formed in 1880 and includes members of the Prussian and Anhalt Governments.

In 1909, owing to dissension amongst the producers and in order to maintain the price of potash and prevent wastage, the Potash Law was passed. This remains in force until 1925, regulates the minimum quantity to be produced for home consumption and the total amount to be exported, provides authorities for apportioning the quantities to be produced by each mine, and fixes the price, per unit of potash, for material exported.

According to recent information the control of the German potash industry is now vested in a Board composed of thirty members (with an equivalent number of deputy members), representing the interests of the producers, merchants, Potash Syndicate, potash miners and officials, agriculturists and the manufacturers of potash products. The representatives of the employers and workmen form a majority on the Board.

Since 1915 the official prices for potash in Germany have been very considerably increased, as shown by the following table, which gives the price in pfennigs per unit of potash per metric ton [7] [164]:

	1918 ¹		1919	
	Home consumption potash (K ₂ O).	Export potash (K ₂ O).	Home consumption potash (K ₂ O).	Export potash (K ₂ O).
Carnallite with 9 to 12 per cent. K ₂ O .	3,900	—	3,900	—
Raw salts with 12 to 15 per cent. K ₂ O	336,000	21,600	370,000	42,100
Fertilizing salts with 20 to 22 per cent. K ₂ O	119,100	63,800	121,600	68,000
Salts containing from 30 to 32 per cent. K ₂ O	19,700	2,000	4,900	660
Salts containing from 40 to 42 per cent. K ₂ O, including fertilizer salts with 38 per cent. K ₂ O	255,100	36,500	9,460	26,600
Potassium chloride	149,800	6,900	301,500	5,650
Potassium sulphate with over 40 per cent. K ₂ O	27,200	1,300	7,220	23
Potassium magnesium sulphate	7,800	5,400	2,060	4,650
Total	918,600	137,500	820,640	147,683

[5] [6]

¹ During the year the total quantity allocated was increased to 1,251,800 metric tons.

Potash (K₂O) sold from the German Mines, by Countries, 1913-19, in Metric Tons.

Country.	1913. ¹	1915. ¹	1916. ¹	1917. ¹	1918. ²	1919. ³
Europe :						
Germany	604,283	520,211	680,561	834,382	859,716	637,033
Belgium	15,234	10,764	10,609	14,434	21,320	115
Holland	43,674	29,065	56,850	43,841	23,828	30,699
France	42,437	59	1	1	—	—
United Kingdom	29,419	—	—	—	—	10,278
Austria-Hungary	28,301	19,497	28,486	32,492	36,741	2,434
Italy	7,320	474	—	—	—	—
Scandinavia and Denmark	34,134	34,027	43,280	27,760	45,608	56,011
Russia and Baltic Provinces	24,568	1,477	3,659	997	4,785	62
Spain	8,355	229	—	—	—	359
Other countries	5,319	4,070	8,506	6,900	9,666	3,234
	843,044	619,873	831,952	960,807	1,001,664	740,225
North America, including Hawaii	248,295	5,046	—	—	—	70,129
Central America	370	23	—	—	—	38
South America	2,549	692	—	—	—	—
Africa	4,370	110	—	—	—	104
Asia, including East Indies	9,194	643	35	36	—	798
Australia	2,547	—	—	—	—	—
Grand Total	1,110,369	626,387	831,987	960,843	1,001,664	811,394

¹ *The American Fertilizer Handbook, 1920.*

² *German Kalisynicate.*

tion of the higher grade potash salts. For further information on the German potash deposits and their working, references [165], [173] and [174] should be consulted.

France.—As a result of a boring made for coal at Wittelsheim, in Alsace, potash deposits were located in 1904. These borings reached a depth of 1,129 metres, rock salt being found at 358 metres, but the presence of potash was not discovered until later, when further borings were made which showed that the potash deposit was of some considerable extent. The two beds so far located lie in the south of the province in the plain bounded on the south by the Jura, on the west by the Vosges, and on the east by the Rhine. Recent borings have shown that secondary beds of the same formation occur beyond the Rhine. The more important of the two beds, which occurs at a depth varying from 650 to 1,000 metres, has an average thickness of 4 metres and an area of 200 square kilometres. The amount of potash averages 30 per cent. of potassium chloride. The second bed occurs about 15 to 25 metres nearer the surface, almost parallel to the first-mentioned bed, to which it is inferior both in area and thickness. Its content of potassium chloride averages about 35 per cent. According to Kestner [1/p. 294] the two deposits lie nearly horizontal, but other authorities state that they are folded and irregular [8]. As the beds are not subject to infiltration of water no concessions are required for the disposal of mine water.

Work so far has been chiefly confined to the lower deposit, the upper strata being mined in only a few places.

It has been estimated that the total cubic content of the two beds amounts to about 1,472,058,000 tons of salts having a content of about 22 per cent. of potash (K_2O), equivalent to 300,000,000 tons of actual potash, enough to supply the world for over 200 years at the present rate of consumption.

The potassium salts occur chiefly as sylvite in alternating red and grey bands, the potash being found in larger amount in the former, whilst the latter consist chiefly of rock salt.

The crude salts are of considerably higher grade than those obtained from the Stassfurt district, and the quantity of magnesium salts and other impurities present is low, therefore

the salts can be used for fertilizing purposes without previous refining, whilst the preparation of a high-grade potassium chloride is simple and cheap, as no potassium sulphate is present.

*Analyses of Alsatian Crude and Manufactured Potash Salts.*¹

Salt.	K ₂ O.	KCl.	NaCl.	K ₂ SO ₄ .	MgSO ₄ .	CaSO ₄ .	H ₂ O.	Insol.
Kainite (Sylvinitic) .	15	22-24	62-65	—	0·15	2·5	1·15	10·2
Manure salts .	20-22	32-34	53-55	—	0·16	2·1	1·34	9·4
„ „ „ .	30-32	49-50	38-39	—	0·10	1·5	1·00	7·2
Muriate of potash .	50	81·3	9·7	—	0·80	—	1·80	6·4
„ „ „ .	52	85·8	7·6	—	0·70	—	1·90	4·0
„ „ „ .	56·5	91·1	4·5	—	0·60	—	1·80	2·0
„ „ „ .	59·6-60	97·3	2·0	—	0·20	—	0·30	0·2
Sulphate of potash .	50·6	—	1·35 ²	93·65	0·80	0·90	2·10	1·2

¹ MgCl₂ nil in each case.

² Na₂SO₄.

The first shaft for obtaining potash was started in 1910 by the Gewerkschaft Amélie, several affiliated companies being also formed shortly afterwards in order to profit by the regulations of the German potash kartel, which allowed a given output for each company working 1,800 hectares. In 1911 the control of the Amélie Co. passed to the Deutsche Kaliwerke, of Stassfurt. At a later date the Société Thérèse was formed by French and Alsatian capitalists to work concessions covering 5,000 hectares. This company has sunk two shafts to the deposit, and two more are in course of sinking.

On the eve of war the four chief groups carrying on operations comprised (1) the Amélie, Max, Elze, Joseph, Marie and Marie Louise corporations, which were absorbed some years ago by the Deutsche Kaliwerke, of Stassfurt; (2) the Theodor and Prinz Eugen corporations belonging to the Gewerkschaft Wintershall, of Heringen on the Werra; (3) the Franco-Alsatian group of Vogt, which controlled the Sté. Thérèse, Alix, Rudolph and Battenheim companies; (4) the Reichsland and Anna companies controlled by the Hohenzollern (Roechling) group of Freden on the Leine. Of the 106 concessions made, 78 were under the control of the Deutsche Kaliwerke, and the remainder under the Société Thérèse [9].

At the time of the signing of the armistice, the capital invested in the Alsatian potash industry was divided as follows: German and Alsatian Government capital 55 per cent.; French capital 25 per cent.; Alsatian capital 20 per cent. [151/p. 1109].

The following details of borings made in Alsace may be of interest [10]. The potash bed was struck in the neighbourhood of Reichweiler by the Max Co. at 1,610 ft., whilst at the Marie and Louise mines in the same neighbourhood the bed was found at 2,210 and 2,275 ft. respectively, 10 to 20 ft. in thickness, dipping at 18° , and having a potassium chloride content of about 40 per cent. Potash was struck on the Elze and Joseph concessions at 1,648 and 1,690 ft., whilst it was found at 1,788 and 1,855 ft. on the Theodor and Prinz Eugen concessions at Wittelsheim in a bed having an average content of 25 per cent. of potassium chloride. The Reichsland concessions have two shafts which met the potash beds at 1,740 ft., the upper and lower beds containing 22 to 25 per cent. and 18 to 20 per cent. of potassium chloride respectively.

At Ensisheim the Alsatian group of financiers has sunk two shafts on the Alix and Rudolph concessions, which cut the potash beds at 2,045 and 2,110 ft.

Production at the Société Thérèse mines had just commenced at the outbreak of war; at the latter period of the war all four shafts were flooded. Little damage appears to have resulted, and in this respect the mines differ from those of Stassfurt, where flooding appears to necessitate permanent abandonment of the mines. The Amélie mine, which was one of the largest producers before the war, has a large plant for the recovery of high-grade potash salts, which was damaged during the war, but is now in working order. The Reichsland mine, which was in better condition as regards the mine workings and refinery, is producing raw and refined salts.

The Alsatian potash works are equipped with modern plant, and some have installations for the manufacture of high-grade potassium chloride. The pit-heads are all connected with the railway, and the mines and works are supplied with electric power from Reinfelden.

The following table gives recent outputs of crude salts in Alsace :

	Metric Tons.		Metric Tons.
1913 . . .	355,341	1917 . . .	320,131
1914 . . .	325,886	1918 . . .	333,499
1915 . . .	114,358	1919 . . .	500,000
1916 . . .	204,474	1920 . . .	1,110,000

The output during 1920 was distributed as follows : France, 450,000 tons ; United States, 327,000 tons ; Belgium, 117,000 tons ; Great Britain, 92,000 tons.

The present output is being provided by 18 works producing the crude salt and by 3 potassium chloride refining plants.

The possible future annual production of the mines already equipped in Alsace appears to be very considerable. It is estimated that each fully equipped shaft should have a hauling capacity of at least 800 tons daily, and on this basis the shafts already equipped would have a daily capacity of 15,000 tons of crude salt. This quantity would be roughly equal to the world's pre-war consumption of potash. It was estimated at the time of the armistice, however, that at least two years would be required to repair and bring these present shafts to their full producing capacity.

Descriptions of the potash mines of Alsace and their working will be found in references [151], [157] and [161].

During 1913, drilling was in progress near Belfort, with a view to locating an extension of the Alsatian deposits. Wells were sunk at Chavannes-les-Grands, Charnesis and Suara, but so far no results have been announced.

Holland.—Saline deposits carrying potash are reported to occur near Wessel, in the province of Overijssel. So far as can be determined no production has been made, and the deposits are somewhat difficult of access.

Denmark.—According to recent information potash deposits have been found at Scherrebeck, Denmark, at a depth of 220 metres.

Poland.—The Austrian Potash Syndicate—which consisted of the Austrian Government and a group of capitalists—controlled the Galician potash deposits in Kalusz until 1913, when a local company took over the control. The deposits were only of local importance, the annual output of about 1,000

tons being insufficient to supply the demands of the former Austro-Hungarian Empire, for in 1913, 21,000 tons of potash (K_2O) had to be imported from Germany. The four beds of kainite and sylvite vary in thickness up to 20 ft., and are stated to be lenticular in form. The average content of potash (K_2O) is stated to be about 10 per cent.

In March 1921, it was reported that the output, which was at the rate of 5,000 wagons per annum, could be increased tenfold if wagons and transport were available. Additional capital has been authorized in order to develop the mines further. For a description of the deposit reference [175] should be consulted.

Potash deposits are stated to occur in the Steppenitz district of Eastern Galicia, but so far no production has been recorded [179].

Russia.—From time to time occurrences of workable potash deposits in Russia have been reported, but little information is available as to their extent or value. It was stated in 1917 that considerable deposits of potash had been located by a scientific expedition near Solikamsk, in the Perm district [12]. According to certain authorities the salts appear to contain from 5 to 7 per cent. of potash, an amount hardly sufficient to prove remunerative in ordinary times; but other accounts credit the raw material with as much as 20 per cent. of potash [13].

A communication published in Essen by a German geologist also refers to the occurrence of potash deposits in Russian Poland. Before the war it was known that the potash-bearing *Zechstein* extended from Germany not only into Silesia, but also into Poland and West Prussia.

Spain.—Deposits of potash salts were found some years ago in the salt district of Cardona in Catalonia, in folded strata considered to be of Tertiary age. They have been prospected chiefly near the town of Suria, to the south-west of Cardona, where borings have been made. The results obtained up to 1914 have been described by C. Rubio and A. Marin [14]; from their account the following details were obtained.

In the valley of the Riera de Tordell the salt deposit is covered by marls. Between these and the potash deposits

there are interposed deposits of gypsum and salt. During prospecting operations several borings were made. One of these reached a depth of 197 ft. and struck the deposit of potash salts at 125 ft. Another reached 380 ft. and began to enter the bed of salt at 182 ft. In a third, salt was met with at 164 ft., and boring was stopped at a depth of 558 ft. in pure white salt. Various seams of carnallite, mixed very irregularly with salt, were encountered. In another boring thin beds of carnallite were traversed at a depth of 426 ft., and boring was stopped at a depth of 886 ft. in white salt. A shaft sunk through the surface marls struck salt at a depth of about 223 ft. At about this depth a cross-cut and a vertical boring were made. The cross-cut passed through anhydrite into carnallite. The carnallite was found in irregular beds, sometimes so broken up that it formed mere patches in the rock salt. The latter occurs in beds separated by fine leaf-like deposits of anhydrite (the typical "year rings" of the Germans). These beds of anhydrite are from 4 to 8 mm. ($\frac{1}{8}$ to $\frac{1}{3}$ in.) and those of rock salt from 2 to 30 cm. ($\frac{3}{4}$ to 12 in.) thick. At the end of the cross-cut, a horizontal boring of about 85 ft. has been made. In both the horizontal and vertical borings carnallite occurs, sometimes in seams of pure mineral and sometimes mixed with rock salt. Sylvite appears at the bottom of the vertical shaft in two bands, whilst in the horizontal boring of the cross-cut it is mixed with masses of carnallite. According to observations made in the cross-cut there is a total thickness of 13 ft. of carnallite and 23 ft. of an intimate and irregular mixture of rock salt and potash salts. These zones of mixture are so irregular that it is not safe to assume that they contain more than 30 per cent. of carnallite. In the horizontal boring there appears to be a total thickness of 48.9 ft. of carnallite and 39.2 ft. of sylvite. An accurate estimate cannot yet be made as to the proportion of potash salts in these veins. On a conservative basis, however, it may be assumed that the carnallite veins contain 50 per cent. of the pure mineral, and that those described as consisting of rock-salt and potash minerals carry 20 per cent. of the latter. On this basis the gross thicknesses of the potash minerals may be estimated to be as follows :

Cross-cut and Horizontal Boring

	Feet.
Rich carnallite	13·12
Mixture (estimated as equal to pure mineral)	6·89
Other potash-bearing beds	24·44
Sylvite	19·58
	} 44·45

Vertical Boring

	Feet.
Carnallite, 72 ft., equivalent to pure mineral	36·0
Carnallite and rock salt, 121 ft., equivalent to pure mineral	30·25
Sylvite, 19 ft., equivalent to pure mineral	4·75

On the whole, the average thicknesses of the beds of potash minerals encountered may be estimated as follows: Carnallite about 56 ft.; sylvite 12·3 to 13·1 ft. The results obtained by borings are as yet inadequate to afford a satisfactory basis for calculating the cubic contents of these beds.

From observations hitherto made it is estimated, on a conservative basis, that in the Suria district the potash beds occupy an area of not less than 75 acres, whilst the total area probably largely exceeds this figure. The carnallite of Suria is deep red in colour and has much the same average percentage of potash as the Stassfurt mineral. Various specimens have been analysed with the following percentage results:

Potash	K ₂ O	12·50	15·26	12·30	11·52
Magnesia	MgO	10·07	13·06	12·02	9·38
Chlorine	Cl	44·70	41·50	41·50	46·70
Sulphuric anhydride	SO ₃	1·07	0·46	0·82	0·71

Other specimens gave the following percentage results:

Potassium chloride	KCl	24·22	20·68
Sodium chloride	NaCl	36·40	39·80
Magnesium chloride	MgCl ₂	17·00	5·50

These analyses indicate that the carnallite is not pure, but rather a mixture with sylvite and sodium chloride.

In Cardona the deposits occur in the axis of a sharp anticline some 220 yards from the town, close to the River Cardoner. The upper beds are interbedded with gypsum and clay, and are much folded and fractured. These deposits are known locally as the Mountain of Red Salt, on account of

their characteristic colour, although beds of white and transparent salt also occur. Below these beds a large compact mass of transparent and very pure white salt is found, which is that principally mined. Formerly it was obtained by open workings, but underground mining is now resorted to, the shaft being 160 ft. deep and sunk entirely in the salt. Potash salts had not been previously recognized at Cardona, but search was made for them after the discovery at Suria, and nearly pure crystalline sylvite, varying in colour from a white transparent variety to one of a more reddish tint, was found. Specimens have been analysed with the following results :

—		White.	Red.	Red.
		Per cent.	Per cent.	Per cent.
Potash ¹	K ₂ O	63·2	62·19	61·97
Magnesia	MgO	nil	trace	trace
¹ Equivalent to potassium chloride (KCl)		98·9	97·1	96·56

The works at Cardona are traversed by a small stream, the waters of which are highly charged with salts. It is calculated that 15 tons of salt per day are lost by this means. Samples of this water were found on analysis to contain from 10 to 48 grams of potash (K₂O) per litre, indicating that a large quantity of sylvite probably exists in the Cardona salt beds.

Concessions to prospect for potash are limited to an area enclosed by Solsona on the north, and Tarrega, Cervera and Manresa on the south, the entire district being practically confined between the Segre and Llobregat rivers [11/p. 616]. In July 1914 a Bill was presented to the Cortes by the Minister of Public Works making the exploitation of the deposits subject to State intervention. The Bill provided for the imposition of special conditions in favour of the home consumption of potash salts, and decreed that a mine producing potash may not suspend its operations so long as the mineral can be mined, unless the operations are being conducted at a loss or for certain other reasons.

A royal decree, published on October 1, 1914, directed that

the State might reserve the right to exclude concessions on free lands, and that the Ministry of Public Works might designate for the purpose of investigation such lands as may be productive of marketable mineral substances used as fertilizers. The Geological Institute of Spain was to designate the lands or zones which should be reserved or investigated. The lands in the provinces of Barcelona and Lérida have been investigated by the Geological Institute, and all lands enclosed by the perimeter indicated by the towns Balaguer, Tarrega, Igualada, Manresa, Vich, Berga and Isona, and amounting to about 1,800 square miles, are reserved to the State.

During 1918 it was announced that the Spanish Government had evolved a scheme for controlling the working of the potash deposits in Barcelona and Lérida, which had much in common with that in force in Germany. Concessions for the mining and sale of the salts are to be subject to Government control. The price for home consumption and export is to be fixed annually as well as the maximum and minimum production for each mine. Suspension of working a concession will only be permitted under certain circumstances, but *concessionaires* are to be allowed a period of two to five years for the investigation and development of a deposit. When the annual output from the Spanish deposits exceeds 50,000 tons, an office in connection with the development, manufacture and sale of potash salts is to be established.

The original concessions, made to a Franco-Belgian group (Sociedad Macary y Viader), include deposits in Suria and Cardona, and appear to be amongst the most important. The concessions comprise an area of 12,000 hectares, and in 1918 the workings included twelve shafts varying in depth from 300 to 850 metres, the area in which the beds are most favourably situated for working having a width of about 10 kilometres. A description of certain of the boreholes has been given by E. M. Heriot [15]. A shaft, which should yield about 1,000 tons of salts per day, was nearing completion at the end of 1918, and it is anticipated that the salts obtainable will carry at least 12 per cent. of potash (K_2O). Three shafts have been sunk near Cardona by the Sociedad de Industrio y Comercio [1/p. 293]. Concessions are also held by the German

Potash Syndicate, several Spanish companies and one group of American capitalists.

Although the Spanish deposits extend over a considerable area, the potash does not occur so regularly as in the beds at Stassfurt and Mulhouse (Alsace). Working would also appear to be more difficult owing to the beds being somewhat steeply inclined.

According to a recent publication, the amount of potash in sight in the Spanish deposits is too small to be of international importance. Estimates for the area prospected place the quantity of carnallite at 2,550,000 tons and of sylvite at 1,150,000 tons compared with 20,000 million tons, the estimate for the Stassfurt basin. For further information see references [14] and [158].

India.—Potash minerals, occurring in regular deposits, have been recorded from several localities: notably the Mayo mine at Khewra, and Nurpur, in the Salt Range, Punjab. The deposits of potassium nitrate described later (*see* p. 40) cannot be accurately described as being of mineral origin.

In 1873, while a set of samples of salt from the Mayo mine was being prepared for transmission to the Vienna Exhibition, it was observed that a certain band of *kallar*, or impure salt, through which a drift was being excavated, had an unusual hardness. Further examination showed that this band, which had a thickness of about 6 ft., consisted of sylvite, kieserite, *langbeinite* (anhydrous double sulphate of potassium and magnesium, $K_2SO_4, 2MgSO_4$) and common salt; the total quantity of material then obtained amounted to only about half a ton. Little attention seems to have been paid to the occurrence until about 1912, when the Geological Survey of India continued the investigation of the deposit. Detailed accounts of the deposits have been given by W. A. K. Christie [16] and M. Stuart [17].

The potash beds at the Mayo mine are generally overlaid by seams of marl, above which occur seams of salt, which are mined by the Northern India Salt Revenue Department. In these circumstances the potash bed is not often exposed. In the Pharwala section of the mine, the principal bed carrying potash minerals has been traced for a distance of about 850 ft.

along its strike and 250 ft. along its dip, which is about N.30W., with an inclination of 20° to 50°. This bed has an average thickness of 6 ft. and carries from 6.8 to 9.6 per cent. of potash (K_2O).

In the Buggy section of the Mayo mine, the only seam of any importance found has an average thickness of 2 ft. 9 in., and carries 14.4 per cent. of potash (K_2O). The seam thins out when followed upwards along the bedding, and at a distance of 170 ft. from the nearest exposure it has a thickness of only a few inches.

The Nurpur deposit is situated in a small salt mine in the gorge of Nilawan, about eleven miles from the railway at Lilla. The principal potash-bearing seam, which is exposed at only one place, is about 6 ft. thick, dipping in a S.E. direction at about 75°, and having a strike N.40°E. The seam has a true thickness of about 6 ft., the potash minerals being chiefly langbeinite and sylvite, but there also occur small amounts of kainite and *blödite* (sulphate of magnesium and sodium, $MgSO_4, Na_2SO_4, 6H_2O$). A further seam has also been located, but both this and the preceding are stated to be very irregular and difficult to work.

During 1916 a small quantity of salts carrying about 14 per cent. of potash (K_2O) was excavated from the Nurpur deposit by the Northern India Salt Revenue Department, and during 1919 about 83 tons of potash salts, valued at £42 at the mines, was produced. An examination of numerous other outcrops in the Nilawan ravine failed to locate potash deposits of any probable importance.

In the table (p. 22) is shown the composition of average samples from the Pharwala-Sujawal, Buggy and Nurpur seams, the first three analyses being by W. A. K. Christie, whilst the last was made in the Scientific and Technical Research Department of the Imperial Institute.

It is remarked that considerable difficulty would be experienced in obtaining pure potash salts from mixtures such as are represented by the analyses (p. 22). Owing to the difference in mineralogical composition, methods of treatment now employed in Europe would probably prove to be inapplicable.

According to M. Stuart the salt was deposited in zones

—		Pharwala- Sujawal.	Buggy.	Nurpur.	
		Per cent.	Per cent.	Per cent.	Per cent.
Potassium	K . . .	8.0	11.9	11.3	8.79
Sodium (calculated)	Na . . .	21.5	10.0	9.2	16.75
Magnesium	Mg . . .	4.8	8.9	9.0	6.06
Calcium	Ca . . .	—	—	—	0.26
Chlorine	Cl . . .	37.5	23.3	21.4	29.69
Sulphuric acid	SO ₄ . . .	22.9	39.3	39.5	31.12
Water	H ₂ O . . .	4.9	7.1	9.3	7.09
Insoluble matter	. . .	—	—	—	0.26

corresponding to those recognized at Stassfurt. He suggests that the uppermost zone, corresponding to the German carnallite zone, has been removed by overthrust, and the three lowest of the Indian zones he names in descending order—the Khewra, Warcha and Kohat. So far, no potash deposits of any importance have been located in the Kohat zone, traces only being found at Nandrakha and Kalabagh. M. Stuart considers that the salt deposits to the west of the Indus will not yield potash on a commercial scale.

At the Warcha salt mines in the Shahpur district there is a seam of potash salts of some thickness, but it thins out in depth. It is suggested that this occurrence may be worth further investigation.

M. Stuart [17] states that, although a certain amount of potash will always be found in the Khewra and Warcha zones, the present distribution is so irregular that no continuous bed of potash is likely to be found anywhere in the Salt Range, and that the recovery of potash salts can here only prove remunerative as a by-product in salt mining.

Canada.—In Cumberland county, Nova Scotia, important deposits of common salt are worked at Malagash. In connection with these is a lenticular deposit of potassium chloride in the form of sylvite in a halite matrix. The potash zone, which varies in width from a few inches to 5 ft., has been encountered at two points, 30 feet apart. The amount of potassium chloride present in the crude material varies considerably; two different samples giving 1.16 and 8.7 per cent. of potash respectively [159].

Abbyssinia.—A deposit of high-grade potash salts was dis-

covered in 1911 by an Italian resident of the colony of Eritrea, at Dallol, in Southern Dancalia, about forty-six miles inland from the Red Sea settlement of Fatimari, and about ten miles from the Italian frontier of Eritrea. The deposits are stated to occur in a barren and waterless district, and this may have been the reason for their not being worked until 1914. Transport difficulties were considerable, as conveyance by camel was the only means then available. In 1914 an Italian company was formed to work the deposits, and it was reported that a force of 8,000 men was then employed in making a road to the coast and constructing a wharf at Fatimari. The salts had then to be sent to the port by camel, at a cost of 250 francs per ton, and were conveyed from the port either by lighters to a steamer, or sent by dhows to Aden or Massowah for trans-shipment [18]. Recently a light railway, 46 miles long, has been built from Fatimari to the nearest point on the Abyssinian boundary, and a 10-mile motor road beyond it to the deposit. Recent outputs in metric tons of 95 per cent. material have been: 1916, 2,500; 1917, 3,578; 1919, 934; and 1920, 1,087. The salts have been exported to Italy, France, Great Britain, Japan and the United States.

The deposit, which occurs in a salt plain having an area of about 482 square miles, lies mostly in a depression 200 ft. below sea-level. At the surface is found potassium chloride of about 90 per cent. purity, the quantity of this salt being estimated at about 140,000 metric tons. The lower layers carry from 40 to 80 per cent. of the chloride, and have been estimated to be equivalent to 1,860,000 tons of 95 per cent. potassium chloride. The working of the deposit has been considerably facilitated by the ease with which a high-grade salt can be obtained, but the cost of the product is considerably increased by the high transport charges. Considerable variation occurs in the composition of the salts: at some points of the deposit sodium chloride predominates, but in all cases the quantity of magnesium chloride is low, and traces of bromides have been found to occur in only a few cases. The waters of the thermal springs of Dallol, which emerge at a temperature of 80° to 90° C., consist of saturated solutions of magnesium

chloride, together with appreciable quantities of magnesium bromide and traces of sodium chloride [19].

Nigeria.—The preparation of salt from saline earth is a native industry in certain parts of Nigeria, particularly in the Manga district of the Northern Province. It may be noted that the term "potash" seems here to be applied to certain native-prepared salts which contain, at the best, little more than traces of that substance. Numerous analyses made at the Imperial Institute have shown that such material usually consists of "sesquicarbonate of soda" ($\text{Na}_2\text{CO}_3, \text{HNaCO}_3, 2\text{H}_2\text{O}$).

A description of the methods of preparing salt from alkali soils has been given in the Reports of the Mineral Survey of Northern Nigeria for 1904-5 and 1906-7 [20].

In the following table is given the composition of certain salts, prepared by native methods from impregnated soils, which on analysis at the Imperial Institute were found to contain notable quantities of potash :

—		1	2	3	4
		Per cent.	Per cent.	Per cent.	Per cent.
Potassium chloride	KCl . . .	4.67	10.00	8.2	7.72
Sodium chloride	NaCl . . .	14.98	43.94	81.00	61.51
„ sulphate	Na_2SO_4 . . .	37.45	27.85	—	23.17
„ carbonate	Na_2CO_3 . . .	2.36	—	1.5	2.44
Magnesium sulphate	MgSO_4 . . .	—	8.55	—	—
Insoluble matter	38.60	7.42	5.5	2.88
Water	1.47	1.82	—	2.12

1. Sheddano salt, Manga district, West Bornu.
2. Pieski salt, Manga district, West Bornu.
3. Salt prepared from Brine Springs at Awe.
4. Salt from Bilma, French Territory.

So far as can be ascertained, none of these salts has been used as a source of potash, but the deposits from which they were obtained might be worth detailed examination.

Peru.—A deposit containing potassium chloride has been reported to occur at Santa Ana, district of Singuas in the province of Arequipa. The deposit, which is probably a lake bottom, occurs in an arid plain about twelve miles from the coast, but the nearest ports are Quilca and Chala, fifteen miles distant.

The potassium chloride occurs about 1 ft. below the surface, under a more or less soft conglomerate, in a deposit about 1 ft. 6 in. thick, carrying potassium chloride about 49 per cent. ; sand 24 per cent. ; sodium chloride 20 per cent. It has been estimated that at least 5 million tons of such material is available in this deposit. Labour is stated to be abundant and cheap in the district.

According to M. Machado [21] salt deposits carrying some potash occur on the plain of the Camarones, between Arica and Zapiga. The deposits occur under a hard conglomerate rock, which is 3 to 5 ft. in thickness. A preliminary examination of the deposit did not give very promising results, few of the samples showing more than 1 or 2 per cent. of potash.

In 1918 rich deposits of potash were reported to occur in the Maco plantation in the province of Jauja [22].

CHAPTER III

SALT LAKES AND PANS

IN many arid regions lake basins occur from which the water has wholly or partially evaporated, leaving the salts previously carried in solution. These salts have crystallized out in approximately the reverse order of their solubility, and as potassium chloride is much more soluble in saline solutions than either sodium chloride or sodium carbonate, the potassium salts are usually found in the residual liquor that impregnates the crystalline sodium salts in these lakes. During the war important quantities of potassium salts were produced from this class of deposit in the United States and Tunis.

United States.—Many areas of this character occur in the western portion of the United States, being there termed "desert basins," and a large number of them have been examined for potash salts [23]. As it is impossible to predict whether any given lake basin will yield potash salts, it is necessary to make trial borings, and to analyse the salts and brines obtained. Many such occurrences have been examined in the United States, the results of which will be found in the numerous publications on the subject issued by the United States Geological Survey. In several deposits potash salts have been located in quantity sufficient to pay for working.

During the years 1916 to 1920 the quantity of potash (K_2O) produced in the United States from such sources amounted to 3,994, 20,652, 39,716, 21,590 and 37,515 short tons respectively [3], [177].

The possibility of recovering potash on a commercial scale from the numerous salt lakes in the United States depends upon a number of factors, such as location, by-products obtainable, etc., and is not determined solely by the amount of potash

in the raw material. This may be illustrated by reference to the following table, which shows the percentage of potash of a number of such deposits, those which have been utilized as sources of potash being marked with an asterisk [3].

Locality.	Material.	Potash (K ₂ O).
		Per cent.
*Jesse Lake, Nebr. . . .	Brine with 19 per cent. salts . . .	5.96
*Searles Lake, Cal. . . .	Saturated brine	2.48
*W. Nebraska	Average from 13 lakes	1.91
Soda Lake, San Luis, Cal. . .	Saturated brine	1.62
*Salduro, Utah	" "	1.24
Death Valley, Cal. . . .	" brines (14)	0.59
*Great Salt Lake, Utah . . .	Brine with 20 per cent. salts . . .	0.41
Little Alkali Lake, Oregon . .	" " 11 " "	0.41
Saline Valley, Cal. . . .	Saturated brine	0.35
*Owens Lake, Cal. . . .	Brine with 11 per cent. salts . . .	0.28
*Sea water (mean of 77 analyses of ocean water) . . .	" " 3½ " " "	0.04

One of the most promising of such deposits is that of Searles Lake (or Borax Flat), California. This "lake," a dry basin similar to many others which occur in the western arid region, consists of a broad, somewhat circular valley, lying between the Slate and Argus mountains, in the extreme north-west of San Bernardino county. The salt deposits occupy an area of about 12 square miles and attain a maximum depth of 100 ft. For many years the lake has been an important source of borax, and more recently of sodium carbonate. The surface of the lake consists of white crystalline salts, which extend to a depth of about 75 ft. and are succeeded by saline muds and sands, the latter sometimes more or less cemented.

At the centre of the deposit the surface is sufficiently hard to permit of motor roads being built upon it.

The crystallized salts appear to occur in horizontal layers varying considerably in composition. The surface layer, which consists of sodium chloride, is succeeded at a depth of 15 ft. by a very distinctive mineral known as *hanksite* (Na₂CO₃, 4Na₂SO₄), whilst towards the bottom occur layers of crystalline *trona* (Na₂CO₃, NaHCO₃, 2H₂O). All are saturated with a brine, which probably occupies about one-fourth of the entire volume, and is here the most remunerative source of potash salts. It

is estimated that the brine contains over 20 million tons of potash (K_2O) [4].

Analyses of the brine obtainable from six wells in the lake, at 30 to 40 ft. below the surface, showed an average content of about 33 per cent. of salts. The average composition of these salts is given in the following table, in which they are shown calculated to the conventional hypothetical combinations [26/p. 613]:

		Per cent.
Potassium chloride	KCl	12.07
Sodium chloride	$NaCl$	51.61
Sodium sulphate	Na_2SO_4	19.22
Sodium carbonate	Na_2CO_3	12.79
Sodium baborate	$Na_2B_4O_7$	3.23
Sodium arsenate	Na_3AsO_4	0.17

The original brine contains a varying percentage of sodium bicarbonate, which is included with the sodium carbonate in the above analysis.

Although potash had been shown to occur in the lake brines as far back as 1898, and the salts had been worked for borax and sodium carbonate for some years, it was not until 1913 that the project of extracting potash received adequate financial assistance. In the previous year, it had been shown from results of examinations made by the United States Geological Survey and the Bureau of Soils, that the brine obtained by borings in the basin contained a high percentage of potassium chloride. The deposits have now been connected, by twenty-five miles of rail, with Searles, on the Mojave-Owneyo branch of the Southern Pacific Railway. Commercial working has shown that potassium chloride, borax, soda-ash, sodium chloride and sodium sulphate can be recovered on a large scale at a fair profit. It has been stated that nearly 15 million dollars has been invested in developing the industry.

The deposits are being worked by four companies, the Solvay Process Company, West End Chemical Company, Burnham Process Company and the Trona Corporation. The brine utilized by the latter company is pumped from six wells drilled in the salt crust, the pumps delivering about 500,000 gallons of brine per twenty-four hours. The brine passes through a series of single- and triple-effect evaporating pans, where sodium sul-

phate, chloride and carbonate separate out, and are removed to the waste salt cones. When sufficiently concentrated, the liquid is run to crystallizing vats, where it cools slowly for about eight days. At the end of this period, the separated crystals are removed, drained and dried, whilst the mother liquor is returned to the evaporating pans, which treat 250,000 gallons of brine and 100,000 gallons of mother liquor each twenty-four hours.

For several years the potash salts sold for fertilizing purposes by the companies working Searles Lake contained up to 3 per cent. of borax, but as trials indicated that borax was harmful to plant growth, the quantity present in the products sold was considerably reduced.

The U.S. authorities have placed such restrictions on the use of potash salts as will prevent the application of more than 2 lb. of anhydrous borax per acre. Producers are forbidden to sell potash salts as fertilizers which contain more than $\frac{5}{100}$ of 1 per cent. borax, or mixed fertilizers with more than 2 lb. of borax per ton, unless the contents are clearly indicated.

The compositions of crude brine and commercial potash salts now sold by the American Trona Corporation are shown in the following table :

		Brine.	80 per cent. Salts.	90 per cent. Salts.
		Per cent.	Per cent.	Per cent.
Sodium chloride	NaCl	16.50	12.45	3.40
Sodium sulphate	Na ₂ SO ₄	6.90	2.14	2.76
Sodium carbonate	Na ₂ CO ₃	4.70	1.04	1.33
Sodium baborate	Na ₂ B ₄ O ₇	1.50	0.40	0.34
Potassium chloride	KCl	4.75	79.84	88.35
Moisture		—	3.99	3.79

The production of the crude potash salts is carried out at Trona on the south-east edge of the lake. About 50 tons of potash salts and 25 tons of refined borax are being produced daily.

The American Trona Corporation during 1917 produced 14,730 tons of crude potash salts and 516 tons of refined potash salts, and in 1918 the amount recovered was 23,000 short tons of crude potash salts containing 13,000 tons of

potassium chloride. According to A. de Ropp [25], in 1918 alterations were being made in the process which would result in a production of 4,500 tons per month of salts carrying 75 to 80 per cent. of potassium chloride and less than 3.5 per cent of borax.

Evidence, given by A. C. Harrigan [27] before the Commission on Mines and Mining of the U.S. Senate, indicated that the costs of production per ton of 100 per cent. KCl salts at Searles Lake early in 1918 were as follow:

	\$		\$
Steam plant	19.60	General overhead expenses	3.75
Labour	6.03	Sales expenses	3.50
Brine	0.52		
Plant, overhead	3.85		
	30.00	Total costs	37.25

A ton of salts carrying 80 per cent. of potassium chloride would therefore cost \$31.25, but to this must be added freight to consumers and other charges amounting to \$17.72.

Fuel has been the chief expense in the past, but this item is now being reduced by a more extensive use of solar evaporation in spray ponds, which averages in depth about 6 ft. per year. Solar evaporation is employed by two of the Searles Lake companies for preliminary concentration of the brine, and a third company claims to produce refined potash salts and borax solely by this means.

A good account of the refining process now used at Searles Lake has been given recently by L. W. Chapman [166].

In north-west Nebraska potash salts occur in various quantities in the salts and brines of numerous alkali lakes, especially in Cherry, Sheridan, Box, Butte, Morrill and Garden counties. The areas of these lakes vary from an acre up to more than two square miles. During 1920 about 45 per cent. of the potash produced in the United States was obtained from such lakes in north-west Nebraska.

One of the largest of these is Jesse Lake, three miles north of Hoffland, which has an area of about 240 acres. This lake received attention as a possible source of potash in 1911, but production on a commercial scale did not commence until 1915. About the middle of 1917 it was claimed that

the production of high-grade potash salts amounted to over 18,000 short tons per annum. The surface brines carry from 12.3 to 14.1 per cent. of dissolved salts, of which potash comprises from 26.4 to 34.8 per cent. The brines utilized are those occurring in the bed of the lake under a thin layer of *hard pan*. The brine is pumped through a pipe-line to the plant on the railroad at Hoffland, heated, passed down a solar tower, and thence to triple-effect evaporators. When its specific gravity has been raised to 30° Bé, it is passed to single-effect evaporators where part of the salts is removed, the liquid being concentrated to 48° Bé, and run to crystallizing vats. The salts produced, which are largely sulphates and carbonates, and contain about 27 per cent. of potash (K_2O), are then run to rotary driers and reduced to a dry clinker-like mass.

Another company is working the brine from Cook Lake, which is situated about one mile north-west from the railroad at Lakeside, where the evaporating plant is situated. Here again the chief source of the rich brine is the porous stratum at the bottom of the lake, the surface liquors during most seasons being too weak to repay evaporation. The rich brines are treated in a manner similar to those from Jesse Lake (*see above*), and yield a product of much the same composition.

Two companies have evaporating plant on the railroad at Antioch, one utilizing the brine from Taylor Lake, three miles to the east, whilst the other treats brine from several small lakes occurring about three miles to the north.

It is reported that about 12 million dollars have been invested in the Nebraska potash industry, the prospects for which are still uncertain. At the conclusion of hostilities the industry received a severe check, due to consumers not buying in the expectation of obtaining relatively cheap potash from Europe. The Nebraska producers were left with about 70,000 tons of mixed salts on hand, which were unsaleable except at a price below the cost of production, and further production was temporarily suspended. However, the expected foreign supply of potash failed to materialize, and not only were the stocks in hand disposed of, but production was actively resumed at many of the plants in the latter half of 1919 [60].

The recovery processes have already been much altered since the industry was commenced, and further improvements are constantly being effected as the result of experience gained in working.

In Utah at least two companies have recovered potash salts from the water of Great Salt Lake. One was formed to treat the waste mother-liquor of the salt works near Potash Siding, whilst the other treats the lake water directly.

The lake water contains about 20 per cent. of dissolved solids, of which about 76 per cent. is sodium chloride, whilst the potassium chloride amounts to about 2 per cent.

The waste from the salt works near Potash Siding consists of a saturated solution of sodium chloride and sulphate, together with potash salts equivalent to from 2.5 to 3 per cent. of potash (K_2O). By evaporation and fractional crystallization a salt carrying from 9 to 12 per cent. of potash is obtained.

The plant of the company treating the lake water is situated at Grants, on the Western Pacific Railroad. The brine is evaporated by solar action in clay-bottomed troughs, until the potash content of the mother liquor is about 4 per cent., when it is separated from the deposited crystals of salt, etc., further evaporated and fractionally crystallized. It does not seem probable that this project will long survive the competition from imported fertilizer salts.

Salduro Salt Marsh lies on the main line of the Western Pacific Railway, 109 to 116 miles west of Salt Lake City, Utah. The deposit, which covers about 125 square miles, on the surface resembles Searles Lake, but the salt crust is only 3 to 5 ft. deep, being underlaid by an undetermined depth of saline mud saturated with brine. The solid matter in the brine carries: sodium chloride, 81; magnesium chloride, 9; potassium chloride, 7; and sodium sulphate, 2 per cent. The plant of the Utah Salduro Company, erected in 1916, and since extended, produces a high-grade potassium chloride. The two products sold contain 85 and 25 per cent. of potassium chloride respectively. The company has a capital of \$2,000,000 [162].

Owens Lake, California, which has been worked as a source of sodium carbonate, has also received attention on account

of its potash content. The lake has an area of about 97 square miles, and an average depth of 29 ft., the brine carrying in solution about 11 per cent. of salts, including about 0.2 per cent. of potassium chloride. The principal salt recovered is sodium carbonate, which constitutes about 45 per cent. of the total solids in solution, whilst a potash salt is obtained from the mother liquor. The process used for the recovery of the potash from these liquors has been described by C. Elschner [29] and L. W. Chapman [166].

The production is stated not to exceed one ton of potash per day, whilst the operating costs are relatively high [28].

Descriptions and references to the other numerous lakes in the United States, which have been found to contain potash, will be found in the *Mineral Resources of the United States for 1915-19*.

In 1920 potash salts obtained from natural brines in the United States amounted to 130,683 short tons, of which amount 85,245 short tons were obtained from the Nebraska lakes, whilst those of California and Utah produced 30,868 and 34,905 tons of crude salts respectively [177].

India.—So far, no potash salts have been produced from salt lakes or brines in India. The salts obtained from the Lonar Lake, in the Buldana district of Berar, Central Provinces, have been stated to contain from 4 to 10 per cent. of potash (K_2O) [30]. According to later investigations, however, there seems to be some doubt as to the previously reported high content of potash in the salt, as samples of the lake water examined in 1911 showed only 0.009 per cent. of potassium in a total of 8.4 per cent. of soluble salts. This would be roughly 0.1 per cent. calculated on the soluble salts [31].

The lake, 94 acres in area, which has been worked on a small scale for many years past as a source of sodium carbonate, at its period of lowest level has a depth of about 2 ft.

China.—The brine obtained from the numerous wells of Tzelinching, Szechwan province, is stated to contain over 1 per cent. of potassium salts. The mother liquor remaining after the crystallization of the sodium chloride is said to contain over 3.5 per cent. of potash.

Tunis.—During the war a dry salt lake, Sebkhah el Melah,

situated to the south-west of Zarzis, and having an area of about 60 square miles, was worked for bromine and potash. The liquor beneath the salt crust of the lake has the following composition in grams per litre: potassium chloride, 13; sodium chloride, 158; magnesium chloride, 141; magnesium sulphate, 32; magnesium bromide, 224 [167].

Potash was also recovered during the war from the mother liquors obtained at the salt works of Mégrine. The potash was separated by precipitation with fluosilicic acid, which was obtained as a by-product from the superphosphate works at El Afrane, but later this process was abandoned as being too costly.

A form of carnallite (*sebkhainite*) has been recovered in quantity from the salt deposits of Sfax and Zarzis. It is stated to have the following percentage composition: potassium chloride, 19.5; sodium chloride, 10; magnesium chloride, 27.2; magnesium sulphate, 9.3; water and insoluble matter, 34. This salt was treated at El Henèche, and gave products containing from 35 to 95 per cent. of potassium chloride.

The factory, which was worked by the French Government, produced between 1917 and 1919 the following amounts of potassium chloride: 1,200 tons of 32 to 35 per cent.; 720 tons of 65 to 67 per cent.; and 280 tons of 85 to 87 per cent.

About 1,000 tons of bromine was also obtained. Production ceased with the end of the war.

The Tunisian Government during the war erected at Aïn-es-Serab, near Zarzis, works capable of producing annually: common salt, 150,000 tons; 50 to 60 per cent. potassium chloride, 6,600 tons; and bromine 800 tons. The works were only recently completed.

Morocco.—Potassium chloride occurs in certain of the Triassic formations of Morocco, but its extraction would probably prove unremunerative. A more promising source in the country is the salt land on the banks of Lake Zima, between Saffi and Marrakech. The soil contains up to 3 per cent. of potash, whilst the lake waters contain about 75 grams of potash per litre [168].

Chile.—Deposits of potash salts have been stated to occur on Huasco Lake in the province of Atacama, and also in the

province of Tarapaca. In 1905 several small companies were formed for the purpose of working these deposits [32].

During 1916 an occurrence in the Pintados Salar, Tarapaca, was examined by H. S. Gale [33]. The Pintados Salar, which is situated in the Pampa del Tamarugal, about fifty miles south-east of the port of Iquique, lies about 3,200 ft. above sea-level, and the Lagunas branch of the Nitrate Railway passes directly through its south-western margin. Its surface is covered with irregular blocks of massive salt crust, averaging about 1 ft. in thickness, underlying which is a granular deposit of several feet. The potash appears to be present as *glaserite* ($(K,Na)_2SO_4$), whilst the granular deposit is chiefly *glauberite* ($Na_2SO_4, CaSO_4$). The area and quantity of salts available in the western half of the *salar*, or saline deposit, are shown in the following table, the area being subdivided according to the percentage of potash present in the samples examined :

Area.	Estimated weight of salts.	Average content of potash, calculated as K_2SO_4 .
Acres.	Short tons.	Per cent.
1,800 . . .	1,650,000	11.6
1,580 . . .	1,760,000	7.4
890 . . .	1,980,000	8.9
1,630 . . .	1,450,000	6.5

Analyses made on samples representing approximately a quarter of a ton gave the following results :

		1	2	3
		Per cent.	Per cent.	Per cent.
Potassium sulphate	K_2SO_4 . . .	—	14.9	10.9
„ chloride	KCl . . .	11.0	—	—
Sodium sulphate	Na_2SO_4 . . .	—	5.9	6.8
„ chloride	$NaCl$. . .	64.3	68.2	75.5
Calcium sulphate	$CaSO_4$. . .	8.0	3.1	1.5
Magnesium sulphate	$MgSO_4$. . .	2.3	3.5	1.0
„ chloride	$MgCl_2$. . .	2.0	—	—
Water	9.8	2.4	0.8
Insoluble matter	. . .	2.0	1.9	3.1

No. 1 represents material from the edge of the salar, whilst Nos. 2 and 3 represent the hard crust from the centre of the deposit.

The extraction of the potash salts from the mixture has been discussed by R. C. Wells [34], who considers that extractions with limited quantities of hot water will probably prove the most suitable method of separation.

Canada.—In certain parts of Saskatchewan, alkaline lakes occur, and these have led to attention being directed towards the possibility of the occurrence of deposits carrying potassium salts in commercial quantities [35]. The water of Quill Lake at Wynward contains 0.016 per cent. of potassium chloride, together with magnesium chloride, 0.562 per cent. ; sodium sulphate, 0.680 per cent., and small quantities of sodium chloride and carbonate, calcium carbonate and sulphate.

Boring for potash was started, late in 1917, in the district between Weyburn and Halbrite, where surface efflorescences of white salts occur during the dry season [36].

CHAPTER IV

POTASSIUM NITRATE DEPOSITS OF MINERAL ORIGIN

Chile.—For many years potassium nitrate has been known to occur, in small amounts, in the Chilian sodium nitrate deposits, but its recovery as a by-product on a large scale was not attempted until the war. Towards the end of 1914 at one works a process was installed for recovering potassium nitrate from the mother liquor remaining after the crystallization of sodium nitrate. The process, which is one of evaporation and fractional crystallization, recovered about one-third of the total potassium nitrate present. The recovered salts marketed consisted largely of a mixture containing about 25 per cent. of potassium nitrate, and the output of the first-named product amounted to about 10,000 tons per annum, equivalent to about 1,200 tons of potash (K_2O). The possibility of a large increase in the quantity of potash recovered from the Chilian nitrate deposits is evident when it is stated that this quantity was obtained by one company, whose output of sodium nitrate amounted to only 1 per cent. of the total Chilian production [37].

According to a recent consular report, the production of nitrate of potash in Chile is being rapidly increased, and sales made for delivery, up to June 1920, totalled 13,500 tons. The potash is made by further refining up to 99 per cent. grade, thus earning a premium of from £1 to £1 10s. per ton over the ordinary 95 per cent. product. So far all sales have been made in the United States [38].

Rhodesia.—Soluble potassium salts have been found here in a banded ironstone. During 1918 two samples of the crude material and one sample of extracted salts were examined in the Scientific and Technical Research Department of the Imperial Institute. The two samples of crude mineral con-

tained 10.0 and 49.9 per cent. of soluble salts respectively. The composition of the salts extracted from the shales at the Imperial Institute and that of the saline matter prepared in Rhodesia, are shown in the following table, in which the constituents are calculated to their hypothetical combinations :

		Salts from crude mineral.			Salts prepared in Rhodesia.
		1	2	3	4
		Per cent.	Per cent.	Per cent.	Per cent.
Potassium sulphate	K_2SO_4 . . .	47.0	46.7	59.0	37.5
„ chloride	KCl . . .	3.3	—	4.1	4.0
Sodium sulphate	Na_2SO_4 . . .	3.5	5.2	4.4	12.7
„ nitrate	$NaNO_3$. . .	5.9	6.6	7.4	2.9
Magnesium sulphate	$MgSO_4$. . .	13.6	37.8	17.2	35.8
Calcium sulphate	$CaSO_4$. . .	26.3	4.0	7.9	5.9

Analyses 1 and 2 represent the soluble matter obtained by total extraction of the shales with water, whilst No. 3 shows the composition of the salts obtained by leaching the crude material No. 1 with six times its weight of water [160].

From the above figures it is evident that the composition of the salts obtainable from the rock is subject to wide variations. No information is available as to the extent of the occurrence or the possibilities of recovering potash salts on a commercial scale.

Russia.—Near Ferghana in Central Asia there occur, in the Eocene formation, certain clay-limestone-sandstones which carry from 2 to 5 per cent. of saltpetre. The deposits outcrop at numerous points in a district rich in fuel and water [46].

Brazil.—Deposits of potassium nitrate have been reported at different places in the valley of the São Francisco River. The saltpetre occurs either in association with other salts on the sites of former ponds or lakes, or in numerous limestone caverns. The remoteness of the district only permits of development to suit local demands [39/p. 217].

The deposits of potassium nitrate about twenty-four miles from Morro do Chapéo, in the province of Bahia, are said to be of very great extent, and to be awaiting exploitation on a

large scale. Analyses of the salt as mined and as crystallized have given: crude, 75 per cent. potassium nitrate; crystallized, 99 per cent., so the material is of very high grade [40].

Venezuela.—Valuable deposits of potassium nitrate are reported to exist near Guanare, in the state of Portuguesa [39/p. 545].

CHAPTER V

POTASSIUM NITRATE DEPOSITS OF ORGANIC ORIGIN

India.—Nitrate is found in the soils of old village sites in various countries; but so far as can be ascertained, India is the only country from which large quantities of potassium nitrate obtained from this source are exported.

The bulk of the Indian exports is obtained from the United Provinces, Bihar (chiefly from Gya, Torhut, Saran and Champaran) and the Punjab, whilst smaller quantities are obtained from Kashmir, Central Provinces, Bombay, Madras and Burma.

The potassium nitrate, which probably results from the combined action of bacteria and air upon nitrogenous organic compounds (urine, vegetable débris) in the presence of calcium carbonate, occurs in the soil mixed with nitrates of calcium and magnesium and sodium chloride. The operation of obtaining potassium nitrate from the soil is usually divided into two stages, viz. (1) the production of a crude nitrate which is sold to a refiner; (2) the refining of this crude material to produce a commercial nitrate. Altogether it has been estimated that there are about 40,000 factories for the production of crude saltpetre in Northern India, and about 600 refineries, but it should be pointed out that the term "factory" may apply to a site worked by only one man.

The collection of the nitrate-bearing earth is carried on from November to the commencement of the monsoon. The surface of the soil is scraped off to a depth of $\frac{1}{2}$ to 1 in., collected into heaps, and then conveyed in head-loads to the factory. The scraping process is repeated at intervals of five to fourteen days according to the rate at which fresh supplies of salts are brought to the surface by capillary attraction. These operations are, in many localities, performed by natives of low caste, called "Nuniah" or "Lunia," but in certain parts

of the Central Provinces and the Punjab the work is carried out by ordinary villagers.

The nitre-bearing earths contain amounts of potassium nitrate varying from 1 to 30 per cent. ; the general average, however, lies between 3 and 5 per cent. The percentage of certain of the principal salts present in earths from various localities is shown in the following table [41/p. 23] :

Source of Sample.	Nitrates of potassium, lime and magnesium.	Sodium chloride.	Sodium sulphate.	Total salts.
	Per cent.	Per cent.	Per cent.	Per cent.
Sewan, Saran, "good" .	7.11	3.85	0.50	11.46
Sewan, Saran, "inferior" .	2.80	1.38	1.45	5.63
Gurwa, Ghazipur, "middling"	4.59	4.34	0.59	9.52
Bhera, Shahpur, Punjab, "good" .	13.08	14.26	6.46	33.80
Bhera, Shahpur, Punjab, "inferior" .	2.41	1.82	1.76	5.99
Mahgaon, Allahabad .	3.42	1.85	1.29	6.56

The method of extracting the salts consists in percolating the earth with a limited quantity of water in a specially-prepared earthen chamber or *kuthia*. The latter is often circular, 5 to 6 ft. in diameter, and 1 ft. 6 in. deep, with a floor sloping from back to front. At the lowest part of the floor, a hole is made in the side of the chamber in order to allow the water to drain out after it has percolated through the soil, which is carefully packed into the chamber to a depth of 6 to 8 in. In order to allow sufficient space for drainage, a false bottom, consisting of bamboos and matting about 4 in. high, is put into the *kuthia*. Small quantities of water are poured on to the earth, and that which percolates through is collected in an earthen vessel, but only the first runnings (*murhan*) are reserved for evaporation. The weaker liquid collected later (*dweji*), which contains too little nitrate to repay evaporation, is reserved for the preparation of *bhinjua* (see below).

The *murhan* is boiled down in open pans over an open fire, the fuel being chiefly dried leaves, the ash of which is employed later in the preparation of *bhinjua*. When the liquid is sufficiently concentrated, and usually before any solid separates from the hot solution, it is transferred to earthenware vessels

to cool and crystallize. The crystals, which consist largely of potassium nitrate and sodium chloride, are sold to the refiner as crude saltpetre. The composition of typical samples is shown in the following table [41/p. 31] :

		Farukhabad.			Mahgaon Allahabad.
		1st quality.	2nd quality.	3rd quality.	
		Per cent.	Per cent.	Per cent.	Per cent.
Potassium nitrate	KNO_3	66.07	65.84	44.92	59.72
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	—	1.96	—	1.28
Magnesium nitrate	$\text{Mg}(\text{NO}_3)_2$	2.54	—	4.80	4.80
Sodium chloride	NaCl	21.84	24.04	35.38	22.04
„ sulphate	Na_2SO_4	3.65	4.36	10.00	2.16
Water		5.00	4.30	3.70	9.10
Insoluble matter		0.90	1.50	1.20	0.90

The nuniah does not attempt to purify further the crude salts (*shora*) or to evaporate the mother liquor, as this would involve the separation of sodium chloride, which he is not permitted to do by the Salt Revenue Department.

The mother liquor (*kahi*) which still contains a considerable quantity of nitrate, is added to the second percolate (*dweji*) mentioned above, and used to treat the residual earth remaining from the first extraction (*sitta*), which is mixed with a certain quantity of the fuel ashes.

The moist earth is spread in the sun and turned over every few days until the soil is dried, an operation usually requiring about three weeks. This material, known as *bhinjua*, forms an important part of the nuniah's stock-in-trade, as a proportion of this is always mixed with the fresh earth or *chhilua* before the latter is extracted. Experiments have shown that rapid nitrification of the organic matter occurs during the preparation of the *bhinjua*. It must be mentioned, however, that the residual earth (*sitta*) is not used immediately for the preparation of *bhinjua*, but is usually stored under cover for one year. After about two months' use the earth composing the walls and floor of the kuthia become impregnated with saltpetre, and are then broken up and used in the preparation of *bhinjua*.

The crude saltpetre is sold to a refiner who holds a licence from the Government to carry on his trade.

The crude saltpetre is refined by throwing it into a boiling solution saturated with sodium chloride and sulphate, but which can still dissolve considerable quantities of potassium nitrate, and so from the crude saltpetre only the nitrates are dissolved. The hot, clear liquid thus obtained is run away from the insoluble salts into vats, and allowed to crystallize. The insoluble salt remaining from the first treatment contains much nitrate, and has to receive further treatment.

The crystallized nitrates are removed from the mother liquor, washed with a small quantity of water, and, after drying, are ready for sale.

The compositions of certain refined Indian saltpetres are shown in the following table :

	Barhanpura Bihar, washed.	Siripur, Saran, No. 1.	Bombay.	"Com- mercial."
	Per cent.	Per cent.	Per cent.	Per cent.
Potassium nitrate KNO_3 .	94.16	90.16	72.46	89.36
„ sulphate K_2SO_4 .	—	—	0.13	0.75
„ chloride KCl .	—	—	6.65	4.57
Sodium chloride NaCl .	1.74	7.64	17.41	0.31
„ sulphate Na_2SO_4 .	—	0.60	—	—
Insoluble matter .	—	—	0.14	0.14
Magnesium nitrate $\text{Mg}(\text{NO}_3)_2$	—	—	0.17	1.97
Water .	4.10	1.60	2.85	2.90
Calcium nitrate $\text{Ca}(\text{NO}_3)_2$	—	trace	—	—

According to published information [41/p. 31], the crude nitrate as then sold to the refineries at Cawnpore fetched about one anna per unit of potassium nitrate per maund ($82\frac{2}{7}$ lb.). When the percentage of nitrate was above 64 per cent. an increased price was paid, and, correspondingly, material carrying 40 per cent. or less was sold at a lower rate per unit. Licences are required from the Indian Government to work nitre-earth and also to refine saltpetre. The price of the former varies with the richness of the soil, and the latter costs Rs. 50.

Full accounts of the occurrence and working of nitre earths

in India have been given by D. Hooper [41/p. 17], J. W. Leather and J. N. Mukerji [42], and C. M. Hutchinson [43].

The last-mentioned author arrives at the conclusions that— (1) the present sources of saltpetre in India are not fully utilized; (2) owing to the methods employed for recovery much nitrate is lost; (3) artificial nitre beds might be installed in Bihar on account of the favourable soil and climatic conditions.

The quantities and destinations of the saltpetre exported from British India during recent years are shown in the following table [44]:

*Exports of Saltpetre from British India*¹
(Long tons)

Destination.	1913.	1914.	1915.	1916.	1917.	1918.	1919.	1920.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
United Kingdom	2,361	2,464	9,112	16,680	23,049	20,406	16,596	5,532
France	51	50	—	—	—	—	447	230
Italy	—	10	24	—	—	—	—	—
Russia	—	—	—	—	517	—	—	—
Ceylon	2,223	2,224	2,409	1,622	53	—	444	4,960
Straits Settlements and Labuan	547	466	249	252	—	—	160	208
Siam	121	137	17	—	—	—	—	14
Japan	—	—	216	384	1,603	1,000	—	622
United States	2,827	1,390	798	499	650	743	5,219	1,679
Hong Kong	4,308	4,034	1,993	883	—	—	352	2,231
East Indies	6	33	17	—	—	—	4	10
British West Indies	75	621	—	—	—	—	—	—
French West Indies	—	250	—	—	—	—	—	—
Mauritius and Depen- dencies	2,261	1,437	1,360	225	319	235	—	2,301
Union of S. Africa	13	214	3	—	—	—	—	74
Arabia and Eritrea	14	27	4	—	—	—	—	12
Australasia and other British Possessions	26	39	195	157	178	298	694	171
Other foreign countries	5	6	1	—	—	—	—	504
Total	14,838	13,403	16,398	20,702	26,369	22,682	23,916	18,548
Total to British Empire	11,814	11,499	15,321	19,819	23,599	20,939	18,246	15,477

¹ Years ending March 31st.

In the following table are shown the quantities of saltpetre produced in the several states of India during recent years [45]:

Productions of Saltpetre from different States of India

(Long tons)

State.	1913.	1914.	1915.	1916.	1917.	1918.	1919.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
Bihar	5,342	4,896	5,673	5,904	5,024	6,300	5,044
Bengal } ¹	197	67	115	276	624	430	—
Calcutta }							
United Provinces	5,758	6,664	7,035	10,743	6,855	11,223	6,616
Punjab	2,964	3,520	5,253	8,140	9,141	6,946	5,661
North-West Frontier	7	2	—	—	—	—	—
Madras ¹	416	254	242	339	274	343	—
Total (British India)	14,684	15,403	18,318	25,402	21,918	25,242	17,548
Central States	24	—	—	25	29	26	47
Cutch (Bombay)	3	1	—	—	—	—	—
Rajputana	363	406	137	244	234	245	180
Total (Native States)	390	407	137	269	263	271	227
Total	15,074	15,810	18,455	25,671	22,181	25,513	17,550

¹ Statistics for years ending March 31st.

The above figures show that the Indian saltpetre industry responded well to the increased demands made upon it for the salt during the war.

Mexico.—Small quantities of crude potassium nitrate are produced by methods similar to those used in India (*see* p. 41). During 1917 and 1918 the amounts exported to the United States were 115 and 62 short tons respectively [169].

Guatemala.—A crude saltpetre is prepared in a number of localities from surface soil in villages. The producing districts are San Augustin, Progreso, and other places in the valley of the Motagua River, Antigua, Occidente and Totonicapan. A good account of the occurrences and method of working has been given by H. S. Gale [171].

Peru.—On the northern coast between Pacasmayo and Huarmey numerous deposits containing potassium nitrate have been reported to occur, many having been worked in the past by natives for the manufacture of gunpowder. The salt appears to occur impregnating a somewhat sandy soil for a depth of 1 to 3 ft. The deposits would appear to be somewhat

similar to those occurring in India, as it is reported that four to six "harvests" can be taken from the same ground each year.

According to information supplied in 1916 by H. B. M. Consul at Callao, the deposits at Huarmey were about to be worked by a Peruvian company holding concessions to work potassium nitrate in several other districts. The deposits, which are situated about 142 nautical miles from the port of Callao, have a workable area of 238,400 square metres, and it has been estimated that each square metre will give 100 lb. of earth, carrying from 3 to 6 lb. of potassium nitrate at each "harvest." The Huarmey deposits were calculated to be capable of giving about 2,500 tons of potassium nitrate per annum. Information from other sources states that after two or three years' working the yield of nitrate from deposits of this character becomes too small to repay operations.

The cost of production of potassium nitrate before the war was estimated to be about \$4 per Spanish quintal (46 kilos.). A plant for the extraction and recrystallization of the potassium nitrate has been erected at the deposit, and the necessary water is stated to be very abundant, and to occur at a depth of 2 metres from the surface.

United States.—Occurrences of potassium nitrate have been recorded from numerous localities, but on investigation most of these have proved to be of little commercial importance (*see* [3/p. 84]).

Rhodesia.—A sample of "saltpetre rock" from a gorge on the Kelewa River, a tributary of the Kafue River in Northern Rhodesia, was examined in the Scientific and Technical Department of the Imperial Institute in 1916. The material, which was found to contain 3.5 per cent. of potassium nitrate, appears to have been derived from the excrement of colonies of baboons. The deposit, which is worked to some extent by natives for the production of gunpowder, is not extensive, and working it on a large scale probably would be unprofitable [160].

Union of South Africa.—From time to time occurrences of potassium nitrate have been reported from certain parts of the Union, notably in the Prieska and Maclear districts [47]. Until a few years ago most of these were believed to be of

limited extent and quite unsuitable for commercial working, but recently important developments have occurred.

The best-known and largest of the nitrate deposits of South Africa occur in Cape Province, near Prieska on the Orange River [48]. In 1895 a small company was formed to work these deposits, but the poor results obtained appear to have been due to the fact that attention was confined to the soil and débris at the foot of the cliffs, whilst the shales were neglected. In 1916, the deposits were brought to the notice of the British Government, and an official investigation was made, but, although the report was stated to be promising, at the time nothing resulted.

In 1918 the matter again received attention from commercial men, and as a result several small interests were amalgamated, and the South African Nitrate and Potash Corporation was formed. This company, which also holds extensive deposits of pyrites, is now in active operation, and apparently intends to build an extensive chemical manure factory.

The nitrate deposits occur in the middle division of the Griqualand beds, which vary considerably in composition.

Where the deposit is hard and silicified, asbestos and magnetite occur, whilst saltpetre is found in the partly-decomposed powdery shales.

It appears probable that the potash is a primary constituent of the rock, and that the nitrification is a secondary process. An examination of a portion of the Prieska district, thirty-three miles long by six miles wide, showed saltpetre in the shales occurring at every farm visited, the quantity present varying from 3 to 30 per cent. The available tonnage is reported to be in excess of the quantity necessary to meet the needs of South Africa.

The thickness of the nitrate shales is stated to average not less than 10 ft., and they are reported to cover a hundred square miles. The shales in many places can be obtained by quarrying, as they usually lie horizontally and are exposed in many places in the valleys cut by the Orange River and its tributaries. In the following table is shown the composition of the soluble matter present in five samples of shale, the results being calculated on the original shale :

	1	2	3	4	5
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Potassium nitrate KNO_3 .	24.3	14.67	5.95	1.2	25.88
„ sulphate K_2SO_4 .	—	10.77	—	—	—
Sodium nitrate NaNO_3 .	—	22.47	—	1.4	1.10
„ chloride NaCl .	—	0.90	1.10	—	0.20
Calcium nitrate $\text{Ca}(\text{NO}_3)_2$	0.30	—	—	—	—
Magnesium nitrate $\text{Mg}(\text{NO}_3)_2$	—	—	2.34	—	—

In order to obtain a marketable product, the treatment process, in most cases, will involve little beyond extraction of the shales with water, evaporation by solar heat as far as possible, and crystallization.

It has been estimated that shales carrying as little as 3 per cent. of potassium nitrate can be mined and treated at a profit, even should the price of saltpetre fall to £20 per ton.

A comprehensive account of the nitrate deposits of the Prieska and Hay districts of Cape Province has been given recently by G. E. B. Frood and A. L. Hall [49].

Upper Egypt.—The soil on the sites of old villages termed *koms* is often employed as a fertilizer on account of its content of potassium nitrate. This material is much valued for this purpose, and is termed *koutri*

CHAPTER VI

SEA WATER AS A SOURCE OF POTASH

ALTHOUGH the utilization of sea water as a source of potash salts has not been carried out to any extent during recent years, owing to competition of the Stassfurt product, it was at one time employed to a considerable extent, notably at the mouth of the Rhone, at Giraud, Camargue, France. At the present time, however, with the enhanced price of potash salts, it might pay to recover the potash from the residues usually run back into the sea from large works for the recovery of salt from sea water, such as exist in France, Portugal, the United States, Australia and India. Sea water contains on the average 0.04 per cent. of potash salts. The world's pre-war output of potash salts from sea water was estimated at about 2,000 tons per annum.

The starting-point in the recovery of potassium chloride is the mother liquor remaining after the crystallization of common salt. Each 1,000 litres of sea water, after removal of most of the salt, gives 64 litres of mother liquor of 27° Bé. (specific gravity 1.231). This is next concentrated by solar heat to 32.5° Bé. (specific gravity 1.29), with the separation of a low grade of sodium chloride. The liquid is next evaporated to 35° Bé. (specific gravity 1.32), when a mixture of salts (*sels mixtes*), consisting of sodium chloride and magnesium sulphate in nearly equal amounts, separates out.

The mother liquor is transferred to deep tanks and kept for some time at a temperature not below 12° C., when magnesium sulphate separates out free from carnallite. At certain works the necessary reduction in temperature is effected by artificial refrigeration. The liquor is further evaporated until, when hot, it has a density of 37° Bé. (specific gravity 1.345). To this is added excess of a hot

solution of magnesium chloride of 40° Bé. (specific gravity 1.383) obtained at another stage in the process, and the whole is well mixed. This causes the separation of a further quantity of *sels mixtes*, which is removed, and the mother liquor, which contains all the potassium chloride, on cooling to about 20° C. deposits carnallite. This salt is treated with small successive quantities of water and washings from a previous operation, thus causing most of the magnesium chloride to pass into solution, whilst the potassium chloride remains behind. This process is capable of giving a product, containing about 82 per cent. of potassium chloride, suitable for fertilizing purposes.

A recent account of the process employed at Salin de Giraud has been given by E. Manzella [50], who states that the annual output from these works averages 800 tons of salt containing 72 per cent. of potassium chloride.

The compositions of certain of the mother liquors which accumulated at works in the United States are shown in the following table [51] :

—		Parts per thousand.			
Potassium chloride	KCl . . .	15.6	25.5	27.8	22.5
Sodium chloride	NaCl . . .	184.2	159.1	62.1	129.7
Magnesium chloride	MgCl ₂ . . .	77.1	84.5	176.3	132.9
Calcium sulphate	CaSO ₄ . . .	4.0	7.4	1.7	3.7
Magnesium sulphate	MgSO ₄ . . .	33.9	39.8	91.5	65.4
„	bromide MgBr ₂ . . .	3.4	3.4	3.4	3.2

Potash salts were produced in 1916 to 1918 from sea water in the United States near San Matéo and Mt. Eden, California.

The mother liquors from the salt works of Trapani, Sicily, are stated to contain about 25 grams of potassium chloride per litre, and it has been estimated that the thirty-two salt works in operation in Italy could be made to yield 2,420 tons of potassium chloride and 194 tons of bromine per annum. The mother liquors from the salt springs in Sardinia have also received attention as a source of potash.

CHAPTER VII

INSOLUBLE POTASH MINERALS

UNDER this heading may be grouped alunite, felspar, leucite, muscovite and glauconite, all of which contain a considerable quantity of potash. The composition of several potash-bearing silicates is shown in the following table [52] :

—		Glauconite from Greensand.	Felspar.	Muscovite.	Leucite rock.
		Per cent.	Per cent.	Per cent.	Per cent.
Potash	K_2O	4·15	12·24	9·77	9·81
Soda	Na_2O	1·84	2·56	2·41	1·37
Alumina	Al_2O_3	6·62	19·10	35·70	11·22
Ferrous oxide	FeO	8·33	—	1·07	1·84
Ferric oxide	Fe_2O_3	15·16	—	1·09	3·34
Lime	CaO	0·62	0·20	0·10	5·99
Magnesia	MgO	0·95	—	—	7·09
Titanic oxide	TiO_2	—	—	—	2·27
Silica	SiO_2	51·56	65·87	44·39	50·23
Sulphuric anhydride	SO_3	—	—	—	0·74
Phosphoric anhydride	P_2O_5	—	—	—	1·89
Water		10·32	0·64	5·88	2·65
Other constituents		—	—	0·42	2·18

It is now generally accepted that under normal conditions the recovery of potash, from minerals in which it occurs in a form insoluble in water, will not prove commercially successful unless valuable by-products are also obtained.

ALUNITE

This mineral at one time was employed almost entirely for the manufacture of alum, but recently considerable attention has been devoted to the possibility of obtaining potash and valuable by-products from it.

Alunite is a hydrous sulphate of potassium and aluminium

approximating (when pure) to the formula $K_2O, 3Al_2O_3, 4SO_3, 6H_2O$. Sometimes the potash is partly replaced by soda (forming natro-alunite), and varying amounts of silica, oxide of iron, lime, magnesia, chlorine and phosphoric anhydride are also present. The colour is white (when pure), but may be cream, pink or red (when impure). According to Dana the hardness ranges from 3.5 to 4, and its specific gravity from 2.55 to 2.75.

The principal occurrences of alunite are at La Tolfa, near Civita Vecchia, Italy; New South Wales; South Australia; and Utah, U.S.A. It also occurs at Montioni, Tuscany; Musaz and Bereghszasz, Hungary; Mt. Dore, France; Western Australia; British Columbia; and on certain islands in the Grecian Archipelago.

South Australia.—Alunite occurs at Carrickalinga Head, on St. Vincent Gulf. The mineral is found near the summit of a headland in nodular masses embedded in a decomposed slate or pug, and lying along the bedding planes of the slate. Similar nodular masses occur in a seam, 20 in. thick, at Myponga Creek, about four miles to the north of the Carrickalinga deposit. The mineral from the latter locality is of exceptional purity, but only 263 tons have so far been raised. The extent of the deposit is not yet known. A recent account of it has been given by R. L. Jack [53].

Near Warnertown, seventeen miles from Port Pirie, a deposit 3 ft. wide has been found, from which 50 tons of alunite have been raised, but the extent of which has still to be proved. Recently alunite was discovered on the sea-cliff of Ramsay, Yorke Peninsula, about five miles from the Port of Stansbury. The mineral occurs in Tertiary rocks as irregular layers from 1 to 10 in. in thickness; the exposure is about 12 chains in length, but it thins out considerably at both ends. Similar deposits may be found in the Tertiary rocks fringing St. Vincent and Spencer gulfs [54]. The quantities of alunite produced in South Australia in 1916, 1917, 1919 and 1920 were 34 (£670), 29 (£145), 60 (£246) and 20 tons (£150) respectively.

New South Wales.—Alunite deposits have been worked for many years near the town of Bulladelah, on the banks of the Myall River which runs to Port Stephens. The mineral

occurs in a narrow mountain range, 900 ft. high and about three miles long, about one-third of which consists of alunite. The high-grade ore is pale pink in colour, and usually carries about 2 per cent. of silica, but it is found only in patches, the rest of the deposit being low grade. Chalk white, purple and granular varieties carry 16.4, 19.5 and 38.5 per cent. silica respectively. The ore is hand-picked, any ore containing over 18 per cent. of silica being rejected, special preference being given to material containing less than 10 per cent. of this impurity.

Large dumps of low-grade ore exist, which could be made to yield from 8 to 16 per cent. of potassium sulphate by roasting and leaching, and it has been suggested that this material might thus be profitably treated and sold locally as a fertilizer. Since 1891 the mineral has been shipped to Runcorn, England, and there employed for the manufacture of alum and aluminium sulphate.

The production of alunite from New South Wales from 1911 to 1920 has varied from 325 tons (1916) to 3,425 tons (1912), and from £1,980 to £17,030 in value.

Western Australia.—A large deposit of natro-alunite has been recently opened up at Kanowna. It is reported to carry about 5.6 per cent. of potash.

British Columbia.—A small deposit of natro-alunite was found some years ago on Vancouver Island, British Columbia, but, judging from the analysis, No. 7, p. 54, it is of little economic value [55].

United States.—Considerable attention has been paid in the United States since about 1915 to occurrences of alunite, the most important of which is that near Marysvale, Utah, where the mineral is being mined to some considerable extent. The mineral has also been found in smaller quantities in Colorado, Nevada, California and Texas.

The Marysvale deposit lies chiefly along the crest of the ridge between the main branch and the north fork of the Little Cottonwood Creek, but the mineral has been also found in many places in the vicinity. The Marysvale alunite may be roughly divided into two varieties; the more valuable kind consists of a pure massive mineral, such as occurs in

Composition of Alunite

	1	2	3	4	5	6	7	8
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Potash	9.51	5.68	6.53	10.35	9.12	7.50	5.60	8.36
Soda	1.12	1.08	0.82	0.89	2.04	1.85	—	1.60
Alumina	37.52	37.37	25.91	35.53	34.99	34.74	19.95	32.98
Ferric oxide	0.26	0.27	0.07	0.34	0.94	0.36	2.05	0.72
Manganous oxide	—	—	—	—	0.16	—	—	—
Lime	nil	nil	0.07	0.10	0.50	0.72	—	nil
Magnesia	nil	nil	trace	0.06	0.29	0.32	—	trace
Silica	1.92	19.34	32.40	1.13	1.87	3.50	52.00	10.10
Chlorine	trace	trace	trace	0.56	0.74	0.11	—	0.42
Sulphuric anhydride	36.76	22.09	24.47	35.61	35.58	35.17	16.00	—
Carbon dioxide	—	—	—	—	—	0.80	—	nil
Phosphoric anhydride	trace	trace	0.02	0.23	—	0.22	—	nil
Water at 100° C.	0.06	0.46	0.16	0.39	—	0.91	—	1.44
" above 100° C.	13.19	13.86	9.65	15.11	13.94	13.85	4.40	14.78

1. Bulladelah pink, N.S. Wales. 2. Bulladelah white. 3. Bulladelah purple. 4. Carrickalinga, S. Australia (2 ton sample). 5. Carrickalinga (1 ton sample, analysis made at the Imperial Institute). 6. Warnertown, S. Australia. 7. Natroalunite from Vancouver Island, B.C. 8. Ramsay, S. Australia.

quantity on Little Cottonwood Creek, whilst the less important variety is composed of more or less crystalline alunite, which occurs disseminated through rocks containing much silica. The Marysvale alunite deposits have been described in detail by B. S. Butler and H. S. Gale [56], and by G. F. Loughlin [57]. These deposits suffer from being a considerable distance from centres of potash consumption and fuel supply.

Italy.—Alunite has been mined for several centuries in Italy, at La Tolfa, for the manufacture of alum. The deposits there have been worked since 1874 by a French company who have produced alum at Civita Vecchia, and aluminium sulphate at Rouen [62].

The principal vein worked has a maximum width of about 33 ft., and has been traced to a depth of 300 ft.

The outputs for the years 1913–19 were respectively: 5,976; 3,700; 4,850; 3,370; 2,455; 2,017; 3,307 metric tons.

Spain.—In connection with alunite, the deposits of the mineral that has been named *calafatite* should be mentioned. This mineral occurs near Benahadux, about ten kilometres from the port of Almeria, and appears to be a variety of alunite. Its composition is shown in column 5 of the table below. As found, the mineral is insoluble in water, has a specific gravity 2.75, hardness 3.5, and is usually of a white colour.

Composition of Alunite (Foreign Deposits)

—		1	2	3	4	5
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Potash	K ₂ O	9.71	7.55	13.80	1.00	9.64
Soda	Na ₂ O	0.56	—	—	—	—
Alumina	Al ₂ O ₃	34.40	27.60	40.00	17.50	37.98
Ferric oxide	Fe ₂ O ₃	trace	1.20	—	—	—
Silica	SiO ₂	5.28	22.71	—	62.25	—
Sulphuric anhydride	SO ₃	36.54	29.74	35.60	12.00	34.77
Phosphoric anhydride	P ₂ O ₅	0.50	—	—	—	—
Water		13.19	11.20	10.60	5.0	17.61

1. Marysvale, U.S.A. 2. La Tolfa, Italy. 3. Montioni, Tuscany, Italy.
4. Bereghszasz, Hungary. 5. Calafatite from Benahadux, Spain.

It is stated that it occurs under a Triassic limestone formation, and several parallel veins have been found having a width of 5 to 6 metres. The working of these lodes is reported to be easy and cheap, and potassium sulphate can be obtained by processes similar to those described for alunite.

The composition of alunite from several localities outside the British Empire is shown in the table on page 55.

Extraction of Potash from Alunite

When alunite is heated to 500° C. it loses its water of hydration, and, if the heating be stopped at this stage, the residue consists largely of anhydrous potash alum. If, however, the heat is increased, then most of the sulphur combined with the alumina is disengaged as oxides, the residue consisting of potassium sulphate and alumina.

It is thus evident that two general methods of treatment are available: (1) to produce potash alum; (2) to make potassium sulphate and alumina; in the latter case, the manufacture of sulphuric acid, as a by-product, is possible.

A method formerly used in Europe for the production of potash alum consists in roasting the coarsely-broken mineral in furnaces somewhat resembling lime-kilns, except that the fuel does not come into contact with the mineral. The roasting is continued for about six hours; the material is then exposed to the air on a clay floor for several weeks, being occasionally moistened. The product is next agitated with water at 70° C., and the clear liquid, which has a density of 10° to 12° Bé. (specific gravity 1.075 to 1.091), is decanted and evaporated to 32° Bé. (specific gravity 1.285). On cooling, potash alum crystallizes out contaminated with a small quantity of ferric oxide. This latter impurity is removed by recrystallization [58].

A larger yield of alum can be obtained by the following process, which involves the use of sulphuric acid [59]. The mineral is roasted for three hours at a temperature of about 800° C., and then added to a predetermined quantity of sulphuric acid, 52° Bé. (specific gravity 1.563), previously heated to 90° C. After being left for two hours, the liquid is

evaporated to 39° Bé. (specific gravity 1.370), and the requisite quantity of potassium sulphate added so as to convert all the aluminium sulphate into potash alum. After being allowed to stand for thirteen hours the clear liquid is removed. The muddy liquid remaining is diluted to 24° Bé. by the addition of mother liquor from a previous crystallization, stirred, allowed to settle, the clear liquid then being drawn off and added to that first removed. The combined solution is allowed to cool for one day, the crystals being removed and purified by recrystallization.

Another method, which has been employed in New South Wales, is the following: The ground mineral is calcined in a reverberatory furnace and then treated with dilute sulphuric acid in lead-lined tanks which are heated by steam coils. The clear solution is run into crystallizing tanks and kept agitated whilst cooling. By this means the alum crystallizes out whilst the aluminium sulphate remains in solution. This latter solution is treated with a further quantity of the calcined mineral in order to neutralize any acidity, and is boiled until a partial reversion takes place accompanied by a precipitation of the iron salts as ferric hydroxide. The solution is then further concentrated until aluminium sulphate solidifies out on cooling. This salt, after grinding, is ready for sale.

The extraction of simple potash salts from alunite has recently received considerable attention, numerous patents having been granted covering many processes, several of which have been employed on a commercial scale. In the opinion of F. K. Cameron [3/p. 117] potash can only be profitably produced from alunite, under normal trade conditions, if the residual alumina in the mineral is sold, and so pays part of the total production cost. So far as can be ascertained this condition has not been attained on a commercial scale.

The deposits of alunite near Marysvale, Utah (*see* p. 53), were opened up before the war with a view to obtaining potash, and the first plant for recovering potassium sulphate was erected early in 1915 by a company in order to work the Chappell process [61]. In this method the mineral is crushed, until its coarser fragments are about the size of large peas, and is then fed into rotary kilns maintained at a temperature

of about 750° C. by means of either powdered coal or oil. By this means sulphur dioxide and trioxide are liberated, leaving a residue of potassium sulphate and alumina, which is digested with boiling water and then filtered. The liquid, which contains the potassium sulphate, is evaporated in triple-effect vacuum pans, and a 95 per cent. potassium sulphate is recovered by crystallization. It was reported, in October 1918, that this plant was producing 600 tons of potassium sulphate per month. The ore used contains about 3.5 per cent. of silica and from 8 to 9 per cent. of potash.

Early in 1921 it was reported that the Armour Fertilizer Works at Marysvale were producing about 50 tons of high-grade potassium sulphate per day.

So far, no use appears to have been made of the residue insoluble in water, which consists of alumina with any silica present in the ore and about 1 to 2 per cent. of potash. It was stated recently that the silica content of this material could be reduced to less than 0.5 per cent. if producer gas were used as a fuel in place of coal, and that the alumina and silica could then be separated by a flotation process.

An interesting account of experiments carried out in Australia on the treatment of alunite from South Australia and New South Wales, has been given in *The Alunite Deposits of Australia and their Utilization* [53], from which the following details are taken.

The changes which take place during the heating of alunite are of some interest. At 500° C. the mineral loses combined water and passes into potassium aluminium sulphate and alumina. The potassium aluminium sulphate is slightly decomposed at 600° C., but the change is only partial even after twenty hours' treatment, but at 700° C. the reaction is fairly rapid, whilst at 800° C. it is rapid and complete, being accompanied by the evolution of copious fumes of sulphuric anhydride (SO₂). If the temperature is maintained at 1,000° C. potassium aluminate is formed. Frequent rabbling of the charge is necessary during the heating, and the evolved gases must be rapidly removed if it is desired to ensure complete conversion into potassium sulphate.

With a view to assisting the removal of the sulphurous

gases from immediate contact with the mineral, the latter was mixed with substances which, when heated, were capable of evolving large quantities of gas.

Experiments were made with sawdust and molasses, the latter being at present a waste by-product of the Australian sugar industry. The molasses was diluted with water and the mineral soaked for some time in the solution, which also served as a binding agent for the finer particles. When sawdust was used, it was mixed with the crushed mineral and water added until the whole was pasty. When Carrickalinga alunite was mixed with 10 per cent. of molasses, the time of heating necessary for complete reaction was reduced from five and a half hours to three hours. Experiments with the more compact Bulladelah mineral showed a reduction from five to two and a half hours. Sawdust was not quite so effective as molasses, but a considerable reduction in the time of heating required was also effected by its use.

The sulphuric anhydride evolved during the roasting of alunite is partly dissociated into sulphur dioxide and oxygen, the percentage dissociated being partly dependent upon the temperature of the furnace, the quantities at 700°, 800° and 900° C. being 53.8, 67.5 and 77.7 per cent. respectively, for the conditions of the experiment.

Leaching experiments showed that material crushed to 1 in. cube size before roasting, leached practically as well as mineral which had been crushed to pass a 40-mesh sieve before heating. It was observed that the majority of the chlorine present in the mineral was evolved and passed away with the sulphurous gases, whilst only traces were present in the residue left after leaching.

In the Morgan process [63], finely-ground alunite is mixed with one-fourth of its weight of lime and heated in a rotary furnace at a temperature of from 640° to 980° C. The lime combines with the oxides of sulphur liberated during the roasting and so prevents the escape of noxious fume. The roasted material is leached with water at boiling temperature so as to obtain saturated solutions, from which potassium sulphate crystallizes out on cooling.

In the preceding processes the object has been principally

to produce soluble potassium sulphate and insoluble alumina, but other processes must be mentioned in which part at least of alumina is rendered soluble.

P. H. Hershman and R. Cooke [64] propose to produce potassium aluminate and alumina by calcining alunite in the presence of steam and carbon, at a temperature sufficiently low to render the alumina soluble in alkali.

FELSPARS AND OTHER SILICATES

Owing to the fact that large quantities of potash felspar can be obtained in many parts of the world at comparatively low prices, the problem of converting the potash in the mineral into a soluble form has received considerable attention, and experimental plants have been in operation at various times in the United States, Canada, Sweden, Italy and the United Kingdom. Important developments occurred during the war in the recovery of potash present in the materials treated in blast furnaces and cement kilns (*see* p. 72). Recent experience has made it fairly certain that in order that a process for recovering potash from insoluble silicates may prove commercially successful, it is necessary that a valuable by-product for which there is a large demand be also obtained.

A useful bibliography of journal articles and United States' patents dealing with the recovery of potash from silicates has been given by E. C. Buck [65] and by H. S. Gale [3/p. 125].

Extraction of Potash from Felspars and other Silicates

The possibility of recovering soluble potash from felspar has received some attention during the past few years, and it is interesting to note that so far back as 1860 a process was tried in this country with satisfactory results. A description of certain deposits in Scotland which contain felspar has been given in Reports of the Geological Survey [66] [67]. During the war several processes were tried on varying scales, but it would appear that these were discarded when blast furnace dust became available as a source of potash (*see* p. 80).

The numerous processes which have been devised for the production of soluble potash salts from silicate rocks have been divided by A. S. Cushman and G. W. Coggeshall [68] into several general classes as set out below. These authors describe a large number of the methods which have been suggested, but only a brief outline of the more typical in each class will be given here, with more recent details of their commercial application.

1. *Natural Agencies*.—Several processes in imitation of these have been tried, such as the action of moisture and carbon dioxide, with and without pressure, but so far as information is available none of these has proved successful.

2. *Treatment with Chemical Solutions*.—The treatment of potash rocks by means of solutions of the alkalis or alkaline hydroxides, with or without pressure, is the basis of many processes [69].

A process for the recovery of potash from greensand with the production of a building material as a by-product, which has been described by H. W. Charlton [70], appears likely to be used on a commercial scale in the United States. The finely-ground greensand is digested with lime and water under 225 lb. steam-pressure for from two to four hours. Under these conditions the greater portion of the potash present in the mineral is set free and forms a solution, from which solid caustic potash can be obtained by evaporation. The potash product is stated to have the following percentage composition: potash (K_2O), 77.2; sulphuric anhydride (SO_3), 0.90; chlorine (Cl), 0.35; silica (SiO_2), 0.70; alumina (Al_2O_3), nil.

The insoluble matter remaining on the filter can be employed in the manufacture of a steam-hardened brick, tile or stone, by incorporating it with a high silica sand, as is done in the case of lime-sand bricks. Greensand is stated to be more suitable for the process than felspar owing to its lower content of soda, and the fact that its alumina does not appear in the soluble portion after the first steam treatment. A large plant operating on the above lines has recently been erected at New Brunswick, New Jersey.

The use of hydrofluosilicic acid followed by sulphuric acid

has been patented [71], as well as treatment with dilute hydrofluoric acid followed by electrolysis of the solution.

Trials have been made in the United States with the Doremus process [72], in which ground felspar is treated in 20 per cent. hydrofluoric acid, giving an insoluble potassium silico-fluoride and a soluble aluminium fluoride, which can be readily separated. Potash is recovered from the insoluble product by heating it to dull redness with gypsum, whereby soluble potassium sulphate is produced. One-third of the fluorine is fixed as insoluble calcium fluoride, whilst the remainder is recovered as silicon fluoride and can be used again.

The chief products of the process, however, are aluminium salts. The solution of aluminium fluoride and hydrofluosilicic acid is treated with aluminous ore to separate the silica, and the aluminium fluoride recovered by crystallization. These crystals when heated in steam give hydrofluoric acid and alumina, the latter in a form available for the manufacture of aluminium or its salts.

A process which is stated to have been used in Germany aims at the production of nitrates. About one ton of potash rock is ground and treated with a solution containing 0.6 ton of basic calcium nitrate at a pressure of four to ten atmospheres for ten to twenty hours. As a result of this treatment the rock is completely disintegrated, and the slime is then systematically lixiviated with water. The solution thus obtained, which contains the alkalies as nitrates, together with a small excess of calcium nitrate, is treated with a small quantity of alkali carbonate, and the clear solution neutralized with nitric acid and evaporated to dryness. It is stated that each ton of rock will give 180 kilograms of potassium nitrate and 220 kilograms of sodium nitrate.

3. *Volatilization of the Potash Salts.*—In these processes the finely-ground rock is mixed with fuel and other substances, and heated so that the potash salts are volatilized. According to a United States' patent [73] felspar is heated with gypsum and carbon, and the volatile potassium sulphate is collected. The production of potash salts as a by-product in cement and in iron manufacture is described on pages 72 and 80.

An interesting process has been worked by the Buffalo

Potash and Cement Corporation of Buffalo, New York, for the production of potash and cement from felspar, limestone and calcium chloride. The process, which is covered by United States' patents [74], consists in charging the correctly-proportioned materials into a water-jacketed blast-furnace of the type used in copper smelting. The potash is volatilized as chloride and caught in dust collectors and a gas-washer, whilst the fused product is tapped from the bottom of the furnace, granulated and ground, giving a cement. Leucitic rock in the Leucite Hills, Wyoming, was worked in 1919. The crushed material was dried, mixed with limestone and salt, heated in a rotary kiln, and the volatilized potash collected in a bag house. The plant was planned for an output equivalent to 8,000 tons of potash (K_2O) per annum [27]. After being in operation for a few months it was closed down owing to technical difficulties.

A process, which has been under trial in Canada at the works of the National Portland Cement Co., of Durham, Ontario, is the following: A mixture consisting of limestone, felspar, calcium chloride and coal is heated in a blast furnace. A fluid slag is obtained, and the potash is volatilized and collected in suitable condensing plant. It is claimed that 90 per cent. of the potash in the felspar is volatilized, and 87 per cent. of this is condensed as chloride, also that the fluid slag can be cast into sewer pipes, tiles or paving bricks. It was stated in May 1917 that a plant was to be erected at Gravenhurst, Ontario, where a large deposit of high-grade felspar exists, and it was calculated that each furnace would want 110 tons of felspar per day, and would give 20 tons of potash (K_2O) and 800 ft. of 20-in. sewer pipe.

4. *Dry Processes for the Separation of Caustic Potash.*—One of these, which was tried by the Societa Romana Solfati, may be mentioned. It consists in roasting the potash rock with carbonate or nitrate of soda or lime or caustic alkali, and subsequently blowing steam through the product in order to produce sodium aluminate and potassium carbonate [76]. The high cost of the operation has, so far, prevented this process from becoming a commercial success.

5. *Dry Processes for Producing Potassium Chloride.*—Many

of the processes included under this heading have been tried on a works' scale, and therefore merit some consideration. In the United States, during recent years several processes of this type have received considerable attention, particularly those which involve the production of a valuable by-product.

Early in 1916, a process invented by J. Rhodin was brought to the notice of the Board of Agriculture by A. C. Auden, who had made experiments with the method in 1913. The process, as described in an English patent specification [77], consists in roasting a mixture of 100 parts of orthoclase felspar with 56 parts of slaked lime and 40 parts of sodium chloride, and lixiviating the product with water. The insoluble matter, which contains about 0.25 per cent. of sodium chloride, is mixed with 40 to 70 per cent. of its dry weight of lime, previously slaked, and the mixture fired at a temperature of about $1,000^{\circ}\text{C}$. The final product is stated to be a finely-divided white hydraulic cement. The results of experiments carried out under Government supervision [78] indicated that by the above process certain felspars would yield about 75 per cent. of their potash in a soluble form, whilst the insoluble matter could be converted into a nearly white hydraulic cement.

The economic possibilities of the process depend upon the price at which the hydraulic cement could be sold, as 27 tons of this product would be produced for each ton of potash recovered. The annual consumption in the United Kingdom of the above type of cement amounted to only about 8,000 tons, but arrangements for disposing of 50,000 tons per annum at 25s. per ton were in course of completion when the investigation was discontinued, as the potash situation in the United Kingdom became less critical.

An interesting process for the recovery of potassium chloride from insoluble potash minerals has been described by E. A. Ashcroft [79]. If orthoclase or microcline felspar be crushed to pass 100 mesh, mixed with its own weight of salt and heated out of contact with air or moisture to a temperature of 900° to $1,000^{\circ}\text{C}$. for several hours, there are formed soluble potassium chloride and an insoluble sodium felspar. The success of the reaction depends upon the equilibrium conditions being carefully maintained. It was found that on an

experimental scale about 80 per cent. of the potash present in a felspar could be recovered as the chloride. It has been suggested that potash could be recovered from the felspar deposits of Sutherlandshire by this process at a profit.

According to recent information, the "Von Kolnitz" process for extracting potash from greensand marl, a hydrated silicate of iron and potassium, was used in 1918 by a company working in Pennsylvania, and resulted in a production of about 150 tons of potassium chloride. In this process the material is heated to a temperature of 335° C. in an oxidizing atmosphere, and then to a higher temperature with calcium chloride in a reducing atmosphere.

A process concerning which there is a fair amount of detail available is that associated with the name "Cushman-Coggeshall" [80]. This process, which has been tried on an extensive scale, consists in treating in a rotary kiln a mixture of finely-ground potash rock and lime with salts of a mineral acid, which when liberated will decompose the silicate.

In practice, 100 parts of finely-powdered felspar are mixed with about 20 parts of lime; sometimes from 10 to 20 parts of salt are also added. The powdered mixture is fed on to the top of a revolving drum, about 3 ft. in diameter, so that a layer about $\frac{1}{2}$ in. deep is formed. Calcium chloride solution is next run on this layer from small tubes, and immediately combines with the lime, giving what may be termed an oxychloride cement in the form of small aggregates or lumps. As the drum revolves a scraper removes the mixture to a belt, which delivers it on a screen where the lumps are separated from the residual powder. This latter is returned to the drum for further treatment. The lumps, which average about the size of peas, are conveyed from the screen to a rotary kiln, similar in construction to those used in the manufacture of Portland cement, and fired by coal dust.

On leaving the kiln, the lumps are practically the same shape as when they entered, but are often stained yellow outside. The heat treatment converts a large proportion of the potash present in the rock into chloride, and little is lost by volatilization. It was proposed to utilize the product as obtained from the kiln, which contains about 7 per cent. of potassium

chloride, as a fertilizer, without attempting to separate the potassium chloride from the other ingredients. A full account of trials, made with 350 tons of felspar, is given in reference [68].

In a later communication [81], Cushman and Coggeshall give the results of further work on the process. It was found that although the cost of production was low, the freight charges on material containing so little potash were a serious drawback, especially as there was little demand in the United States for potash fertilizers of this character. The potash salts in the crude product are readily soluble in water, and a solution containing 10 per cent. of potassium chloride can be obtained by using the wash waters for leaching fresh material. Various methods of concentrating this solution were tried, and the most economical was found to be that of spraying the solution through the waste furnace gases from the kilns. By this means a sludge is obtained which is thoroughly dried in rotary driers. The material thus obtained contains from 70 to 80 per cent. of potassium chloride and 14 to 16 per cent. of sodium chloride. This composition compares favourably with that of commercial chloride. If fractional crystallization be employed a high-grade potassium chloride can be prepared.

The plant required for the above process is somewhat similar to that employed in cement works. It is stated that to handle 300 tons of felspar per day of twenty-four hours, the plant required would include three rotary kilns, each 100 ft. long and 7 to 8 ft. in diameter. In the article quoted, detailed costs of the equipment are given, but it will be sufficient here to state that the part of the plant which is identical with that employed on a cement works would cost \$100,000, and the additional plant required is estimated to cost \$70,000. The authors estimated in 1914 that a product identical with the German "80 per cent. muriate" could have been sold at \$31.3 per ton.

6. *Dry Processes Producing Sulphates.*—Several of these have been patented, and one at least has been tried on a fairly large scale. Experimental work on the commercial extraction of potash from silicate rocks has been carried out at

Curtis Bay, Baltimore, Maryland. It has been stated that the Thompson process [82] is used, in which the rock is ground to pass a 100-mesh sieve, mixed with sodium bisulphate and an alkali chloride. The proportions used are: Felspar rock, 5 parts; sodium bisulphate, 5 parts; sodium chloride, 1.8 parts. The mixture, after being heated to a bright-red heat for one or two hours, during which time it becomes partly fused, is allowed to cool and is then finely ground. On extracting the mass with water, a solution containing sulphates of sodium and potassium is obtained, and these salts are then separated by fractional crystallization. The initial reaction between the substances is supposed to consist in the formation of gaseous hydrochloric acid and normal sulphate; the hydrochloric acid acts on the felspar to give potassium chloride, which in turn reacts with a further quantity of acid sodium sulphate to give potassium sulphate and hydrochloric acid. It is stated that the yield of potash varies from 80 to 90 per cent. of the quantity present in the felspar. To secure efficient working it is necessary to control the temperature within fairly narrow limits.

In addition to the above-mentioned processes, there have also been patented several which involve the production of Portland cement as a by-product. According to calculations by W. H. Ross, each ton of potash (K_2O) obtained by this means would involve the production of about $3\frac{1}{4}$ tons of Portland cement. The chief differences between the present method of making cement and those suggested for the additional recovery of potash salts are: (1) the substitution of felspar for a certain proportion of the aluminous body, i.e. clay, now used; (2) replacing a portion of the limestone by calcium chloride. By this means a large proportion of the potash in the felspar would be volatilized and could probably be caught in the flue gases. The possibilities of the process are discussed by B. Herstein [83], and by W. H. Ross [52].

7. *Miscellaneous Processes.*—A process which cannot be placed under any of the above headings has been under trial in Sweden. The finely-ground felspathic rock is mixed with scrap iron and carbon in certain proportions, and the whole smelted in an electric furnace at a temperature of about

1,800° C. The products obtained are ferro-silicon and a glassy slag containing potassium in the form of a silicate which is more soluble than felspar. The slag is ground in ball mills and afterwards screened. Fertilizer trials with the finely-ground slag, which is sold as "elektrokali," have been made in comparison with potassium sulphate, the amounts employed being such that each product contained the same amount of potash. The results are stated to have been satisfactory, the elektrokali being found about 78 per cent. as efficient as the potassium sulphate.

The following analysis of the elektrokali has been published. The analysis of the rock used (*kalileptit*) is also given for comparison :

		Elektrokali. Per cent.	Kalileptit. Per cent.
Silica	SiO ₂	48·15	71·43
Silicon	Si	5·17	—
Iron	Fe	5·34	0·98
Alumina	Al ₂ O ₃	20·68	14·16
Lime	CaO	5·00	0·06
Magnesia	MgO	1·00	0·45
Soda	Na ₂ O	1·17	1·34
Potash	K ₂ O	11·46	10·72
Carbon	C	1·70	—
Phosphoric acid	P ₂ O ₅	trace	0·05
Titanium dioxide	TiO ₂	trace	0·40
Water	H ₂ O	0·33	0·45

"Kalikalk," a mixture of felspar, limestone and gypsum, which has been calcined at 1,150° C., is sold in Sweden as a fertilizer.

Commercial samples contained 5·6 per cent. potash, 52 to 71 per cent. of which was soluble. Percentages of other constituents were: Lime, 33; soda, 1·7; silica, 37; sulphate, 8 to 10; iron oxide, 1·7. The material has fertilizing properties equal to those of potassium sulphate [152].

A process which involves the production of a fertilizer containing both potash and phosphoric acid has been described by A. H. Cowles [86], and is stated to have been investigated by a company in New Jersey, U.S.A. Potash felspar is ground with rock phosphate in such proportion that the latter supplies two molecular weights of lime to each molecular weight of silica in the felspar. The mixture is sintered at a

temperature of about $1,000^{\circ}\text{C}$., and the resultant product is extracted with sulphuric acid. The substances obtained are insoluble dicalcium silicate, soluble potash alum and orthophosphoric acid.

The quantities of potash salts recovered in the United States from silicate rocks during the years 1916 to 1920 were: 46, nil, 201, 1,307 and 160 short tons respectively.

Although considerable attention has been devoted to the solution of the problem of how to obtain soluble potash from feldspar and similar insoluble silicates, so far as information is available it cannot be said that any considerable quantity of potash has been produced from this source, nor do the majority of processes so far described seem capable of competing, under normal conditions, with salts from the Stassfurt and Alsace deposits.

The exceptions to this generalization, however, are the processes for recovering potash from the flue gases evolved in the manufacture of Portland cement and iron (*see p. 72*).

INSOLUBLE POTASH MINERALS AS FERTILIZERS

During the past few years attention has been directed towards the possibility of employing as fertilizers, with or without previous treatment, minerals and rocks which contain potash insoluble in water. The more important of these are alunite, feldspar and leucite.

Alunite.—The treatment of this mineral for the recovery of alum or potassium sulphate has already been considered (*see p. 56*), and it remains to discuss the value of the mineral itself as a fertilizer. Experiments carried out in the United States in this direction have indicated that when wheat was grown on a Carrington loam, using ground raw alunite as the potash fertilizer, the increase in weight over that obtained on the untreated soil averaged 16 per cent., the fertilizer being applied in amounts equivalent to from 25 to 500 lb. of potash (K_2O) per acre. When the mineral was roasted before being applied and similar amounts were used, the increase averaged 31 per cent., thus demonstrating the superior efficiency of the roasted product. The effect of the ignited alunite was as good as that obtained with potassium sulphate of equivalent

potash content, and superior to that yielded with potassium chloride.

Leucite.—The utility, as fertilizers, of rocks containing this mineral has received considerable attention, notably in Italy. The results of experiments made with leucite rock show that in most cases it is very inferior in its action to soluble potash salts. For equal quantities of potash applied, if the increase in crop induced by potassium sulphate be taken as 100, then the increase induced by leucite rock varies from 4 to 60, averaging 26. It would appear that soils containing much organic matter are more favourable for the utilization of the potash in these minerals than are those of a more sandy character. A useful summary of experimental work on this subject is given by Lemmermann [87].

According to information supplied to the Imperial Institute by the International Institute of Agriculture at Rome, leucite deposits have been worked in Italy on Mount Vesuvius and in the Alban Mountains. An account of some of the Italian leucite deposits has been given by H. S. Washington [88]. At Civita Castellana, where the surface workings cover an area of about 3 sq. km., the rock is crushed, and the leucite separated electromagnetically from the other minerals. The concentrate, which contains about 90 per cent. of leucite, is used for the manufacture of alum and also as a potash fertilizer. At Le Capannelle leucite was formerly separated from puzzolana by sifting. The waste material obtained from either of these processes has been used in the manufacture of reinforced concrete. The output of leucite concentrates from Italy during the past few years has varied between 1,000 and 2,000 metric tons per annum.

According to a report in 1915, it was proposed to work phonolite for fertilizing purposes near Hafnarfjord in the Reykjavik district in Iceland. It was estimated that the output would be about 900 tons per week. Information is lacking.

Felspars.—Numerous comparative experiments have been tried with both leucite and potash felspar. As a general rule, these have proved that felspar is much inferior to leucite as a fertilizer, having in many cases less than half the value, as demonstrated by increased yield of crop.

Mica.—Muscovite and biotite have a relatively high content of potash compared with other micas. It seems to be still a matter to be settled whether these are superior or equal to the felspars as potash fertilizers.

As a general rule, it may be concluded that the employment as fertilizers of minerals containing insoluble potash compounds is not likely to prove remunerative, unless the material is available in large quantity at a low price. Even under these conditions their use may not prove satisfactory.

Minerals containing insoluble potash are employed as fertilizers in Italy, Austria, Russia and Germany, but no statistics are available as to the quantity so used.

CHAPTER VIII

FLUE GASES AS SOURCES OF POTASH

CEMENT KILN DUST

THE possibility of obtaining potash from the fine dust produced during the manufacture of Portland cement has received considerable attention during recent years, particularly in the United States. Raw cement mixtures as a rule contain a small amount of potash which occurs as felspar or other insoluble silicates. Analyses made a few years ago of raw materials from most of the Portland cement works in the United States showed a potash content varying from 0.2 to 1.16 per cent., and that the quantity of potash volatilized at the various works ranged from 0.35 to 5.34 lb. of potash (K_2O) per barrel of cement (380 lb.). The average amount of potash lost was 2.09 lb. per barrel from nine American works, and 1.95 lb. per barrel from nine Canadian works [89]. It has been calculated that this quantity of potash (K_2O) thus escaping with the waste of flue gases from the cement works in the United States is equivalent to 86,850 tons per annum.

The dust obtained during the manufacture of Portland cement in rotary kilns may be roughly divided into two classes: (a) heavy dust, which settles readily and consists largely of unburnt cement mixture; (b) fine dust, which is carried some considerable distance and escapes largely into the air, unless special means are taken to prevent this occurring. It is this latter variety of dust which carries the majority of the volatilized potash.

The fact that potash was volatilized during the manufacture of Portland cement was recorded fourteen years ago by R. K. Meade, but the first plant installed for the recovery of the

fine flue dust was erected in order to mitigate the nuisance which it caused to the orange growers in the neighbourhood of the Riverside Portland Cement Co.'s works at Los Angeles, California. When the valuable nature of the trapped dust was realized, a number of other cement works in the United States and elsewhere installed plant during the war for its more adequate collection.

The quantity and probable potash content of the dust produced at a cement works are important factors when considering the possibilities of the material as a source of potash. It has been stated that the loss of material from cement plants in the United States employing the "dry" process amounts to about 5 per cent., and the dust produced would amount to about 4 per cent. [89]. The quantity of dust produced in the "wet" process is dependent upon many factors, but a fair average will be about 2 per cent. of the material. At one plant, the dust collected in the flues and stacks connecting the kilns with the special dust recovery plant, amounted to 27 per cent. of the total dust produced, and contained 4.5 per cent. of potash. The remaining dust which was saved by the special precipitating plant contained 11.4 per cent. It is thus seen that the finer dust, which under normal conditions of cement manufacture passes into the atmosphere, contains more than two and a half times as much potash as the heavier material deposited in the flues.

The ratio of potash to soda in the dust is a matter of considerable importance in connection with the question of obtaining high-grade potash salts from the dust. Analyses of dust from cement plants in the United States showed that the quantity of potash with one exception exceeded that of soda, the ratios varying from 0.92 to 6.07 : 1 with an average of 2.66 : 1. It has been stated that any cement works whose raw mixture contains over 0.3 per cent. of potash can reasonably expect to make a net profit on dust recovery even in times of a normal potash market [90]. It appears, however, that on account of the cost of the dust recovery plant, the process will not prove remunerative to instal at works operating only a single rotary kiln.

The potash volatilized under ordinary conditions of cement

manufacture varies between 25 and 95 per cent. of the total quantity present in the raw mixture. This wide variation is due in some measure to differences in burning, but variation in the composition of the raw materials has probably a greater influence. According to W. H. Ross, A. R. Merz and C. R. Wagner [89], the average quantity of potash volatilized from cement plants, in the United States, using the "dry" process of manufacture, was 47 per cent., whilst at those using the "wet" process the volatilization was 46 per cent. Contrary to expectation, the two highest percentages (90.7 and 95.9) were recorded at works using the wet process.

Two main problems have to be considered in connection with the recovery of dust rich in potash from cement works: (a) means of increasing the percentage of potash volatilized; (b) the collection of most of the fine dust in a form suitable for fertilizing or manufacturing use.

The possibility of increasing the percentage volatilization of potash from cement materials has received attention from several investigators. Laboratory trials on the influence of temperature and various substances on the rate of volatilization have been recorded by E. Anderson and R. J. Nestell [91]. The experiments showed that the whole of the potash could be driven over at temperatures between $1,200^{\circ}$ and $1,300^{\circ}$ C. if sufficient time were allowed, but at $1,400^{\circ}$ C. the time required was short. Speedy volatilization is a matter of considerable importance, as the cement mixture remains in the hottest zone of the rotary kiln for only a comparatively short time. The speed of volatilization was considerably decreased by the presence of sulphates in the cement mixture, and accelerated by chlorides [83]. The addition of sodium chloride for this purpose is now in use at certain cement works (*see* p. 77), whilst calcium fluoride has also been employed (*see* p. 75); other substances proposed include calcium chloride [92] and steam and sulphur dioxide [96].

In addition to the above methods, the quantity of potash passing from the cement kiln can also be increased by adding some aluminous mineral rich in potash (such as felspar) to the raw mixture in substitution for a portion of the clay. The addition of felspar is only economically possible, however,

where the other raw materials are not highly siliceous and felspar can be obtained fairly cheaply.

The numerous processes which have been devised for recovering the fine dust from the flue gases may be roughly divided into—(a) wet or dry electrostatic methods; (b) wet spray treaters; (c) chamber settling methods. In practice, a combination of two of these methods is frequently employed. These methods can best be illustrated by reference to the processes employed at several cement works in the United States, where potash recovery on a large scale from dust has been successfully undertaken.

The first cement plant to obtain potash as a by-product was that of the Riverside Portland Cement Co., of Los Angeles, California. When it became evident that the recovery of potash from the flue dust could be made a commercial success, the quantity of potash in the raw mixture was increased by selecting for use those portions of the "clay" deposit which were richest in potash and by the addition of felspar. The proportion of potash in the raw mixture was thus raised from 0.2 to 0.8 per cent. The proportionate volatilization of the potash was raised from 60 to 90 per cent. by adding to the raw mixture about 0.8 parts of calcium fluoride for each one part of potash (K_2O) present [93]. During the burning, the insoluble potash minerals in the mixture react with the calcium fluoride at $1,100^{\circ} C.$, to give potassium fluoride, which is very rapidly volatilized and passes away in the flue gases. On its way to the dust collector, however, it comes into contact with partly burnt cement dust and oxides of sulphur, the result of the reaction being soluble potassium sulphate and insoluble calcium fluoride. When at a later stage the collected dust is extracted with water, potassium sulphate passes into solution and the calcium fluoride remains with the insoluble matter, the latter being returned to the kiln with a later batch of raw mixture.

At this plant the flue gases from eleven rotary kilns are drawn to one general treating plant where the Cottrell electrostatic precipitation process is used. The electrostatic method of precipitating finely-divided solid matter from a suspension in a gas was patented in England by Oliver Lodge in 1880. Since that date the principle has been employed industrially

by Lodge in the United Kingdom and by Cottrell in the United States [172]. The Cottrell process consists in passing the dust-laden gases through an intense electrostatic field in which the dust particles become charged and are driven from the high potential discharge to the earthed collector electrode, where they accumulate and whence they are periodically removed. The Cottrell dry treater consists of a number of sheet-iron tubes or channels through the centre of which chains, wires, or rods are suspended, the surface of a tube and the central wire forming the electrodes. The requisite charge is produced by connecting a source of alternating current to the low tension terminals of a step-up transformer, the high tension terminals of which are connected with a mechanical rectifier. This latter instrument changes the alternating current power supplied to it to one of uni-directional polarity of 70,000 volts and delivers it as such to the precipitator. At intervals the current is stopped, and the tubes rapped mechanically to shake down the accumulated dust, which is removed to the potash extraction plant (*see* p. 79). This treatment removes up to 95 per cent. of the total solids present in the gases.

The first cement works to install plant primarily for the collection of potash was the Security Lime and Cement Co., of Security, Maryland. When the dust-collecting system was installed in 1916, it was observed that the ratio of soluble to insoluble potash in the dust was considerably lower than was the case at the Riverside plant. The comparative solubilities of the two materials are shown in the following table :

	Riverside dust. Per cent.	Security dust. Per cent.
Water soluble potash (K_2O) .	9.8	6.8
Slowly " " " .	0.7	4.1
Acid " " " .	0.2	0.5
Total potash .	<u>10.7</u>	<u>11.4</u>

These differences were due to the fact that the fuel used at Riverside was oil, whilst at Security coal was employed, and the silicates in the ash recombined with the potash to give silicates, which were soluble with difficulty in water. An

account of an interesting investigation on the nature and formation of these insoluble potash compounds has been given recently by A. R. Merz and W. H. Ross [94]. In a recent United States patent it is claimed that the insoluble potash in flue dust may be converted to a water-soluble form by ignition in an oxidizing atmosphere. This insolubility has now been largely overcome by adding salt to both the powdered coal and raw cement mixture. This addition also increased the percentage of potash volatilized.

The quantity of salt to be added amounts to about one per cent. of the raw mixture. The addition is stated to have no deleterious effect on the finished cement, which actually contains a lower percentage of alkalis than when no salt is added. The dust-collecting plant in use before the salt process was started consisted of Cottrell precipitators of the tube type, which collected 95 per cent. of the dust; but it was found that when salt was added the efficiency of the electrical precipitators decreased. The loss of dust, however, was more than compensated by the greater richness in potash of the dust collected, and it was stated by R. K. Meade [95], that the loss has now been overcome by the use of a supplementary water-film treater of the Cottrell type. In this plant the wires are located between two walls of concrete, over the surface of which flows a thin film of water which takes the place of the surface of the tube in the treater described on p. 76.

The electrical discharge between the wire and water film carries the dust to the latter. The solids are allowed to settle out, and the water used repeatedly until nearly saturated with salts, which are finally recovered by evaporation. The composition of a sample of the dust recovered at the Security works during 1916 was stated to be as follows [3/p. 136]:

		Per cent.
Potassium sulphate	K_2SO_4	16.7
Potash (present as silicate)	K_2O	3.3
Sodium chloride	$NaCl$	4.0
Calcium carbonate, sulphate and lime	$\left\{ \begin{array}{l} CaCO_3 \\ CaSO_4 \\ CaO \end{array} \right\}$	52.0
Iron oxide	Fe_2O_3	3.0
Alumina	Al_2O_3	6.0
Silica	SiO_2	15.0

The cost of collecting potash at the Security plant in 1917, according to J. J. Porter [97], was as follows :

	Per unit of potash.
	\$
Collection, including labour, power and laboratory	0·14
Packing and shipping	0·08
Salt	0·25
	<hr/>
	0·47
	<hr/> <hr/>

The above operating costs do not include depreciation or royalty. From detailed estimates given by the same author it appears that an operating profit of \$0·4241 per barrel (380 lb.) of cement produced can be obtained from potash recovery, with potash valued at \$4·5 per unit, and if this latter value is reduced to \$1·0 the profit per barrel would be \$0·0605. These estimates take no account of charges for royalty or depreciation of plant.

The ideal procedure for the collection of potash, according to J. J. Porter, General Manager of the Security Lime and Cement Co., would consist in passing the gases, at a relatively high velocity, through a dry precipitator, thus removing 50 to 75 per cent. of the coarsest dust, which would be returned to the kilns. The gases would next go through a water-film treater where most of the dust would be precipitated. The water after repeated circulation would be evaporated by waste heat, whilst the insoluble sludge would be treated in digesters at 100 lb. pressure for one hour in order to recover the recombined potash. The cost of such a plant, in 1917, was estimated at \$150,000 for a 3,000 barrel plant.

The wet-spray method of treatment is employed at the plant of the California Portland Cement Co. The gases pass first through dry settling chambers followed by water sprays, the liquid from which is used a number of times and then employed for leaching dust from the dry settling chambers. This plant has a daily capacity of about 3,000 to 4,000 lb. of potash salts containing 40 per cent. of potash.

A novel system is in use in Utah at a Portland cement works at Ogden, Salt Lake City, where the dust precipitator consists of two large brick chambers which have a number of brick partitions arranged so as to cause the gases to flow alternately

up and down the chambers, sprays being fixed at the top and corners of each compartment. In the first chamber or "saturator" the gases become saturated with water vapour, and in the second chamber or "condenser" the vapours are condensed, carrying in solution the soluble potash which is recovered by evaporation when the solution is sufficiently concentrated.

Another variety of wet process has been devised by J. G. Dean [98] and used at a Portland cement works at Victorville, Cal. Here the wet process of cement manufacture is employed, and the gases which contain 30 to 40 per cent. of water are passed through a condenser. The liquid thus obtained is used as the cooling medium for further hot gases which serve to evaporate the solution. The kiln gases thus effect vacuum evaporation of the liquid. When the solution has been concentrated to a specific gravity of 1.1 the evaporation is continued in open-top steam evaporators.

Several processes have been devised for the extraction of potash from the collected dust; most of these differ chiefly in mechanical detail. The following brief outline of that employed at the Riverside works will be sufficient to give a general idea of the methods employed.

The dust is charged into tanks fitted with stirring gear and containing water at 85° C. [99]. Owing to the hydration of the caustic lime the solution rapidly boils, and the water-soluble potash soon passes into solution. The extraction of each batch occupies about fifty minutes, the end of the process being ascertained by means of specific gravity determinations on the liquid. The temperature of the solution has to be maintained at or above 85° C. by means of steam coils, as it has been found that below this temperature an insoluble compound of potash and lime may separate out.

When the extraction process is complete the solution is run into a filter reservoir where the solid matter is separated by means of suction filter drums. The solution is next run into evaporating ponds and there left until it has attained a specific gravity of 1.1, when it is transferred to evaporating pans. The liquid in these is maintained at constant level, and the salts which separate out are recovered periodically.

A recovery plant to yield 7,000 lb. potash per day, in which the dust is collected by wet-spraying, was erected by the Canadian Cement Co., at Port Colborne, Ontario, in 1920 [163].

Certain cement manufacturers sell the fine cement dust in its crude condition to fertilizer makers for use in compound fertilizers. The material may carry from 4 to 20 per cent. of potash, and probably averages about 6 per cent. It seems likely that when normal conditions again prevail it will be necessary for a product to carry at least 10 per cent. of potash in order to be saleable for fertilizing purposes. This improvement in the grade can usually be attained by selective precipitation. So far as can be judged from data available, the installation of special plant for dust precipitation is not likely to prove remunerative where the product from only one or two kilns is concerned.

In the United States from this source the outputs of "crude potash" (rich dust) in 1917-20 aggregated 48,067 short tons. It was estimated by R. K. Meade [95] that when all the cement dust recovery plants under construction in 1918 came into operation, their annual output would be equivalent to 10,000 tons of potash (K_2O).

In the United Kingdom during 1919 an attempt was made to recover potash from cement-kiln dust at a works in Middlesex [170].

In 1917 it was stated that a company working at Durham, Ontario, was using felspar as an ingredient in the manufacture of Portland cement. In addition to the plants for collecting potash at cement works in the United States, which number about sixteen, installations are also at work in Norway, Spain, Japan and Sweden [100].

Several processes have been tried for the production of potash from felspar with some variety of cement more or less as a by-product. An account of certain of these methods is given under "Felspars and Silicates" (*see* p. 60).

BLAST FURNACE DUST

The gases issuing from the top of a blast furnace during the smelting of iron ore contain a large proportion of valuable combustible matter which is utilized in various ways in the

works. For the majority of uses it is necessary for the gas to be freed from the dust and fume carried over from the raw materials. Analyses of the finer dust and fume have shown that they contain a large proportion of water-soluble potash, which has been produced in the furnace from the silicates of potash occurring in the ores and fluxes. The possibility of recovering potash from blast furnace flue dust has received considerable attention since 1915, both in the United Kingdom and in the United States.

United Kingdom.—It has been estimated by K. Chance [101] that for each ton of pig-iron produced in the United Kingdom, there is fed into the furnace in the raw materials the equivalent of about 15 to 30 lb. of potassium chloride. On this basis the quantity passing annually into these blast furnaces would be about 200,000 tons.

Of this total quantity, under ordinary conditions of working, about 150,000 tons is lost in slags, and 50,000 tons is volatilized with the gases in the form of carbonate, chloride and cyanide, and four-fifths of this is finally discharged into the atmosphere. Part of the remaining 10,000 tons is deposited in the "down catchers" and "down comers" with the heavy dust, whilst a further quantity is recovered mostly as sulphate in the boiler flues and stoves.

It would appear that as a general rule the British ores contain more potash than those imported from abroad, those of the Oxfordshire and Northamptonshire belt being particularly rich, followed by material from the Cleveland and North Lincolnshire deposits. Foreign hæmatite ores appear to contain less than one-third of the available potash found in British ores.

The processes employed for removing dust from blast furnace gas include: (a) wet-spray methods; (b) electrical precipitation; (c) dry-cleaning processes usually involving bag filtration. It is evident that if the maximum recovery of water-soluble potash is required, processes of the first-mentioned type are not suitable (*see p. 78*).

Electrical precipitation (*see p. 76*) has not been, so far, largely employed in this country for this purpose, although it is stated that the Lodge process has been satisfactorily used

for treating 40,000 to 80,000 cubic feet of gas per hour at one works at least [154]. The third kind of process, of which the Halberg-Beth may be taken as typical, has received considerable attention in connection with the recovery of potash from blast furnace dust [102]. It was, in fact, the examination of dust recovered from a Halberg-Beth plant at the works of the North Lincolnshire Iron Co., Ltd., that led to serious attention being directed in this country to this source of potash.

K. M. Chance [103] states: "The recovery of potash in a gas-cleaning plant at a blast furnace has one enormous advantage over all other native sources of supply in that the value of the main product of that plant, namely clean gas, is in itself sufficiently great to provide a handsome remuneration for the capital outlay involved in erecting it and the cost of its operation, so that the cost of recovering potash already in the gas in the form of dust is nil. The second consideration is that the main items of cost in volatilizing potash from an ore in which it is present in insoluble form—namely, cost of raw material, labour and fuel—are, in the case of a blast furnace, already incurred and reckoned as items of cost in the manufacture of the main product, pig-iron, whereas in the production of potash from felspar or alunite, those items of cost have to be borne by the potash unless a market can be found for some by-product which will carry their weight."

The composition of the dust recovered is very complex and will, of course, vary to some extent with the nature of the raw materials used. In the following table is shown the percentage analysis of a sample of dust recovered from the Halberg-Beth plant at Scunthorpe:

Soluble in water.		Per cent.	Insoluble in water.		Per cent.
Potassium bicarbonate	KHCO_3	23.23	Ferroso-ferric oxide	Fe_3O_4	11.68
" carbonate	K_2CO_3	14.66	Calcium carbonate	CaCO_3	10.39
" chloride	KCl	10.90	Zinc sulphide	ZnS	2.23
" cyanide	KCN	5.58	Magnesia	MgO	1.05
" formate	KHCO_2	3.66	Carbon	C	2.18
" sulphate	K_2SO_4	1.13	Silica	SiO_2	8.91
Sodium carbonate	Na_2CO_3	3.97			
Iron cyanide	$\text{Fe}(\text{CN})_2$	0.48			
Zinc and lead as sulphides	.	0.36			

It will be seen that the composition of the dust presents several marked differences from that recovered in the production of Portland cement (*see* p. 72).

It is stated that the dust recovered by the Lodge electrostatic process at the Skinningrove Iron Works, Yorkshire, differs from the above in several material details. Carbonates and cyanides are absent, and only traces of sulphate are present in the dust which contains potassium chloride, 20 per cent. ; sodium chloride, 8 per cent. ; and calcium chloride, 7 per cent [154].

After the question of the most suitable type of gas-cleaning plant has been settled, there remains the problem of decreasing the quantity of potash lost in the slag. Preliminary experiments, carried out under the direction of K. M. Chance, led to two methods being selected for extensive trials. It had been found that the volatilization of the potash as carbonate depended upon the temperature of the furnace, and the ratio of lime to silica in the charge. Increase in these led to a greater quantity of potassium carbonate in the gas, but experience has indicated that the increased working costs would more than exceed the value of the extra potash obtained. The second method, which appears to be commercially possible, is that of adding to the charge an alkali chloride, such as common salt, which thus takes the place in the slag of much of the potash and enables about 70 to 80 per cent of the latter to be volatilized as chloride at the ordinary working temperature of the blast furnace. The evidence so far available shows that the addition of salt has no deleterious effect on the linings of the blast furnace. The quantity of salt to be added has to be determined by experiment for each ore, the desirable quantity being such as will give in the dust a maximum of potash together with a minimum of soda. As a general rule the quantity required is about three-quarters of a ton of salt for each ton of potash contained in the dust.

The quantity of potash that can be recovered from blast furnaces by the combination of the use of salt with a gas-cleaning plant seldom falls below 100 lb. of potassium chloride per million cubic feet of gas, and in certain districts it considerably exceeds this amount.

The British Potash Company was formed for the production of refined potash salts from blast furnace dust, and the first factory has been erected at Oldbury. Factories will be erected in other localities as the production of blast furnace dust justifies. It has been decided that the smallest unit, that can be erected consistent with economy, will be one whose annual output of potassium chloride will be not less than 25,000 tons.

It would appear that the future of this source of supply in Great Britain depends almost entirely upon the installation of dry-cleaning plant for the waste gases at the blast furnaces.

The recovery of potash in Scotland from blast furnace products seems to present several features differing from those occurring in England or the United States. This is due to the fact that whereas coke is the fuel principally used in the two countries last mentioned, in Scotland coal is generally used. As a general rule, the raw materials also contain a smaller percentage of potash. According to R. A. Berry and D. N. McArthur the use of coal causes a somewhat large quantity of tarry matter to be produced, and it is necessary to remove this before the gases can be used in the stoves, the washing being usually done by water. In most works this water, after removal of the tar and ammonia, is run to waste, but at some works it is evaporated by waste heat and its potash recovered. The following balance sheet of the potash charged into the furnaces and that recovered at one blast furnace works in Scotland, together with the possible recovery from the 102 blast furnaces in Scotland, has been given by Berry and McArthur [104].

	Per ton of pig-iron produced.		
	lb.		
Potash (K_2O) charged into furnace	7.6
Potash recovered in spent liquor	1.4
" " " flue and stove dust	0.04
" " " pitch ash	1.7
" " " tube cleanings	0.2

The estimated possible annual production for Scotland is shown in the following table :

Product.	Weight.	Water-soluble potash.	Total soluble potash (K ₂ O).
	Tons.	Per cent.	Tons.
Spent liquor	1,694	35.15	567.4
Flue and stove dust	100	8.0	8.0
Pitch ash	11,092	8.0	885.8
Tube-cleaning dust	8,250	2.5	206.0
Estimated total production			1,667.2

So far as can be ascertained, no important quantity of potash has been recovered from blast furnace dust in Scotland.

United States.—In the United States the question of the recovery of potash from blast furnace dust seems to have attracted less general attention than has been the case in the United Kingdom. This has probably been due to the fact that numerous other sources of potash supply were being worked. The matter received considerable attention, however, at the Bethlehem Steel Works, and a comprehensive account of the investigation made there has been published by R. J. Wysor [105].

It appears that the total quantity of potash present in the raw materials used in that works, which averages 22.4 lb. per ton of pig-iron produced, is considerably above the average usually found in blast furnace materials either in the United States or in this country.

The composition of the dust caught in the several parts of the plant shows great variation in potash content. The gases on leaving the furnace top go through dust-catchers, and deposit the coarser dust, which carries about 0.61 per cent. of potash, about half of which is soluble in water. The gas is next treated in tower spray washers, but, contrary to expectation about 20 per cent. of the potash entering this plant goes through untrapped. A small quantity of dust containing 44.6 per cent. of potash is deposited in the mains leading from the spray washers to the stoves. It is from the passes of the latter that the largest quantity of potash is recovered. The stove dust carries from 5 to 20 per cent. of water-soluble potash, the average of thirty-six car-loads, weighing 1,073 tons, being 9.90 per cent. Where the gas is intended for use in gas engines, it is treated in the secondary wet washers after

leaving the tower spray washers. This removes most of the dust and potash, which is thus lost.

The losses and recoveries of potash in the various parts of the Bethlehem Works have been summarized as follows :

	Per cent. of total potash charged.	Lb. per ton of pig-iron.
<i>Potash recovered :</i>		
In dust-catcher dust	2.7	0.6
In stoves and boiler passes	1.3	0.3
<i>Potash lost :</i>		
In slag	20.0	4.5
In fume from iron and cinder notches	2.0	0.4
In gases from top of furnace	3.9	0.9
In primary washers	55.9	12.5
In secondary washers	2.2	0.5
In mains, stoves and boilers	0.4	0.1

Experiments were made with a Cottrell electrical precipitator installed to treat the gas as it leaves the dust-catcher, and it was found that practically all the dust was trapped. The potash content of the material amounted to about 10 per cent. It is evident that such treatment would increase considerably the quantity of potash recovered by eliminating most of the loss due to primary washers.

During 1918, four steel companies sold potash-bearing dust obtained from blast furnaces. The material carried from 6 to 9 per cent. of potash, and represented dust which had settled in the flues of stoves and boilers. The quantity of blast furnace dust recovered in the period 1917-20 was 8,398 short tons [177].

CHAPTER IX

VEGETABLE SOURCES OF POTASH

At the present time, none of the vegetable sources of potash promises to become a formidable competitor with the mineral sources of supply. Seaweed was used extensively in the United States during the war, but all the plants, with two exceptions, closed down in 1919. Other vegetable sources are only worked at a profit under special circumstances, such as the recovery of potash as a by-product from beet-sugar factories and distilleries, the manufacture of wood ashes in the lumber camps in Canada, and the treatment of sunflower stalks in Russia.

MARINE PLANTS

The ash of seaweed contains a considerable quantity of potash.

Scotland.—The preparation of potash salts from the ashes of marine plants has been carried on in Scotland since 1730. At the beginning of the nineteenth century the output of finished salts from Scotland amounted to about 20,000 tons per annum. Competition with the Stassfurt and Alsace deposits as regards potash salts and bromine, and with those of Chile as regards iodine, has reduced the Scottish industry to small dimensions, though its revival has again been considered [106].

The ash obtained by burning the weed is known as *kelp*, whereas in the United States the product is called *kelp ash*—the term *kelp* being there applied to the fresh weed.

The deep-water weeds are now made use of where possible, as they contain more iodine than those exposed on the shore at low tide. They are chiefly *Laminaria digitata* and

L. Stenophylla, which are cast up after storms. (For a comprehensive account of the seaweeds gathered on the coasts of Scotland, see J. Hendrick [107]). The productions of kelp in Scotland in 1913, 1914 and 1915, amounted to 3,062, 2,500 and 2,100 tons respectively [108].

In South Uist and Benbecula the season lasts from the beginning of May to the end of September. The weeds are dried for two days, and are then turned and dried for another three days. Exposure to rain entails a considerable loss of potash and iodine, and should therefore be avoided as far as possible. The collection and burning of the weeds, which grow between the tide-marks, are carried on from November to March.

An open, shallow kiln, with brick or stonework sides, from 6 to 10 ft. long, 2 to 3 ft. wide, and about 12 in. high, is used for burning, but closed kilns are sometimes employed. The dried weed is laid on a bed of dried heather or straw, and the whole fired. The operation lasts from five to six hours, five tons of dried weed producing one ton of kelp, the composition of which is shown in the following table :

		Kelp burnt to a slag. Per cent.	Kelp burnt to a loose ash. Per cent.
Potassium sulphate	K_2SO_4	13.95	12.71
„ chloride	KCl	17.79	18.09
Sodium chloride	NaCl	14.00	6.80
„ carbonate	Na_2CO_3	3.92	3.43
„ thiosulphate	$Na_2S_2O_3$	0.75	0.17
„ iodide	NaI	0.76	1.48
Insoluble matter	44.80	49.75
Water	4.05	7.00

The kelp, as it is received at the chemical works, is often in the form of large semi-fused lumps and has first to be broken to pieces not over 2-in. cube in size, and is sometimes further ground to a coarse powder by means of edge runners. The lixiviation of the ash is carried out in rectangular iron vats having false bottoms, which are heated by steam. The kelp is repeatedly treated in these vats with water at a temperature of about 43° C. ; the strong liquors obtained in the first treatment are run off to the settlers, whilst the weaker solutions

obtained by the later lixiviations are used for treating further quantities of fresh kelp. The extraction of each batch of kelp is usually continued until the liquids, which drain away, have a gravity of 3.4 Bé. (specific gravity 1.025).

The concentrated liquors which register 24° to 26.4° Bé. (specific gravity 1.200 to 1.225), after being allowed to settle, are transferred to open, hemispherical, cast-iron evaporating pans, each about 9 ft. in diameter. In certain works the evaporation is conducted in the more economical closed pans. These are heated by steam coils and have mechanical agitators to prevent the separated salts from adhering to the sides of the pan. The concentration is usually continued until the liquor has a gravity when hot of 33.3° to 35.4° Bé. (specific gravity 1.30 to 1.325). The hot liquor is then run into settlers, where the salts which have already separated out are allowed to settle, and passes on into cylindrical crystallizing vats. The residue in the settlers contains about 60 per cent. of potassium sulphate, the remainder being sodium sulphate and sodium chloride.

The hot liquor is allowed to cool very slowly over two or three days, and a crop of potassium chloride of about 90 per cent. purity is obtained. The mother liquor from this operation is further evaporated, the mixture of sodium chloride sulphate and carbonate ("kelp salt") which separates during the operation being removed from time to time. The solution is again allowed to crystallize, and a further crop of potassium chloride is obtained. This process is repeated, the "kelp salt" being removed from the hot liquor and the potassium chloride being obtained by crystallization on cooling.

The second crop of potassium chloride often contains 98 per cent. of the pure salt, whilst the third crop usually does not carry more than 82 per cent. The mother liquor remaining is fairly rich in iodine, which is recovered by one of the well-known processes.

The residue remaining after the extraction of the soluble salts from the kelp is used in France as a fertilizer, as it contains a large proportion of calcium carbonate and phosphates of lime and magnesia. According to A. A. Moffat [109] the residue has approximately the following composition :

		Per cent.
Calcium carbonate	CaCO ₃	20.50
„ sulphate	CaSO ₄	3.06
„ sulphide	CaS	1.70
Magnesium carbonate	MgCO ₃	9.11
Salts of potash and soda	1.50
Mineral phosphates	6.72
Carbon	3.09
Silica and sand	20.82
Water	33.50

At one time this residue was used in the manufacture of common glass bottles.

From time to time methods have been suggested for the more efficient working of the kelp industry, particularly in relation to the method of burning and the recovery and utilization of the products evolved during that process. One of the earliest of these was the process, devised by Stanford, of carbonizing the dried weed in closed retorts in order to recover the ammonia evolved and to avoid loss of iodine. In 1863 several works were erected, notably at Locheport, in North Uist, for working the process, but these were unsuccessful owing to technical difficulties, a fall in the price of iodine, and the difficulty of transporting the dried weed to the works.

Ireland.—Kelp is prepared at many places on the Irish coast, and from 1913 to 1918 six counties produced 3,939 (£16,631), 4,320 (£20,520), 4,314 (£23,727), 4,151 (£31,132), 2,491 (£19,928) and 4,818 (£19,000) tons respectively [110]. The percentage composition of a typical sample, showing more potash than the Scottish product, is as follows: potassium sulphate, 11.14; potassium chloride, 27.17; sodium carbonate, 5.82; sodium thiosulphate, 1.22; sodium iodide, 0.82; insoluble matter, 41.41; water, 3.10. During 1916–17 considerable quantities were purchased by a firm in Galway.

Norway.—There were in 1912 nine kelp factories in Norway, the produce being chiefly shipped to England and Scotland for treatment. During 1913, the price paid for kelp was about £8 6s. per ton. The pre-war annual production of kelp ash in Norway amounted to about 1,000 tons, the product containing from 34 to 37 per cent. of potash.

The seaweed most favoured is that known on the west

coast as *skraame*, or *glastare*, which grows below low-water mark. The weed is burnt by starting a fire with a few small pieces of wood, and adding dried seaweed, taking care that the latter does not burst into flame. As the burning proceeds, half-dry and finally wet weed is added to the heap. Usually from 700 to 1,000 kilograms of weed are burnt in each heap, and yield from 150 to 200 kilograms of ash. When the fire has gone out, the unburnt weed on top is removed and the ash spread out to cool. It is not considered advisable to use water to cool the ash.

The quantities of kelp ash, in metric tons, exported from Norway during recent years are shown in the following table :

—	To Great Britain.	To Germany.	Total.
1915	520	15	535
1916	700	97	797
1917	1,331	478	1,809
1918	559	—	559

It was estimated that the home consumption of kelp ash in Norway during 1916 amounted to about 539 metric tons.

Japan.—The preparation of iodine and potash salts from seaweed has become an important industry at certain places on the coast of Japan. It was stated in 1914 that Japan supplied about 80 per cent. of the iodine consumed in the United States. Seaweed is put to many other uses in Japan [111] [113], the weeds mostly used being species of *Laminaria*, *Ecklonia cava*, *E. bicyclis* and *Sargassum* spp.

It would appear that a considerable proportion of the potash recovered from seaweed is converted into potassium chlorate. Early in 1917 it was stated that the production amounted to 10,000 barrels per month, whilst the normal domestic consumption was about 7,000 barrels per month [112]. At the end of 1917 there were forty-nine factories, with a capacity of 10,000 tons per annum, producing chlorate at the rate of 6,000 tons per annum.

No recent information is available regarding the production of potassium chlorate in Japan.

South Africa.—Analyses of certain South African seaweeds have been published by M. Lundie and R. W. Hallack [114], and G. F. Britten [116], from which it would appear that the potash contents of *Ulva lactuca*, *Enteromorpha intestinalis*, *Ecklonia Buccinalis* (stems) are 0.36, 0.77, 1.95 per cent. respectively. According to Marchand [115/p. 1127] the last-mentioned is the only weed which would yield a product of sufficient value to warrant the cost of collection and preparation.

So far as can be ascertained no attempt has been made in the Union of South Africa to utilize these weeds as a source of potash salts.

Canada.—The giant seaweed *Nereocystis* has been observed in varying quantities over a distance of about ten miles on each side of Nanaimo, Vancouver Island [117], and, in 1916, a plant erected near Sydney was treating about 40 tons of wet weed per day. The beds near Cumshewa inlet, Moresby Island, in the Queen Charlotte group, cover an area of about ten square miles, and in 1917 a plant was erected there with a capacity of about 1,000 tons of wet weed per day.

United States.—During the last decade, the subject of recovering potash and other products from marine plants on a scale much more extensive than that of the Scotch and Irish kelp industries has received the attention of the United States Geological Survey and the Department of Agriculture. The giant seaweeds of the Pacific coast, consisting chiefly of the species *Nereocystis luetkeana* and *Macrocystis pyrifera*, exist in enormous quantities, but a regular and adequate supply can only be ensured by systematic harvesting. The potash contents of the above species average 20.1 and 12.59 per cent. respectively of the material dried at 105° C. [155].

One harvesting vessel used on the Pacific coast [118] has a crew of six men, two 60-h.p. engines (speed nine miles per hour), and deck space for 130 tons of weed (two and a half hours' work in a rich region). For detaching the weed there is a horizontal cutter bar 12 ft. long, fitted with oscillating knives, and, at the end of this, are two vertical cutting bars, each 4 ft. long, equipped with similar knives. The horizontal cutter works 4 ft. below the surface, and the

weed as cut is caught by a slat conveyor and deposited on deck.

From data published during the war the cost to harvest, bring ashore, and unload one short ton of wet weed varied from \$0.493 (I. F. Laucks) [119] to \$1.1 (C. A. Higgins) [123].

On exposure to air in single layers these giant seaweeds dry rapidly, and about 50 per cent. of the salts appear as an efflorescence on the surface.

Raw seaweed contains about 90 per cent. of water, and the most economical form of drier is probably one of similar design to the rotary kilns, used for drying fish scrap.

In 1913, F. K. Cameron [120] gave the following estimates for the plant and working costs of treating 500 short tons of wet weed per day: Plant, \$60,000 (including \$25,000 working capital); working costs, \$370 (including \$50 for interest and depreciation). As 500 short tons of wet weed produce 75 short tons of dried weed, the cost of one short ton of dried weed will be \$4.93. Assuming the latter contains 15 per cent. potash it will be worth \$14.75 per short ton (with nitrogen and potash at \$2.5 and 65 cents per unit respectively). The above are pre-war estimates; they would now have to be considerably increased.

The dried seaweed can be used: (1) as a potash and nitrogenous fertilizer, after grinding it to a sufficient degree of fineness; (2) as a potash fertilizer in the form of ash (kelp); and (3) as a source of potash salts and iodine, with the recovery of many by-products as in the Scottish kelp process.

In reducing the seaweed to an ash, the following method has been employed [118]: The weed, on leaving the barge, is passed through a modified form of ensilage chopper which reduces it to about 12 in. in length, and thence to storage bins. The yellowish slimy substance which exudes from the chopped weeds, and is rich in potash, is collected and evaporated by waste heat, yielding a purple crystalline mass containing about 25 per cent. of potash. The wet weed then undergoes a preliminary drying in the rotary driers, which are unlined steel-plate cylinders, 42 ft. long and 7 ft. in diameter, and inclined about $\frac{1}{10}$ in. per foot towards the discharge end. Twelve rows of hooks, fixed to the interior of the cylinders, serve to

lift the wet weed and then drop it through the heated air of the drier. Feeders supply each drier with 15 lb. of wet weed every fifteen seconds. The heating is by oil burners. The gases on meeting the wet weed have a temperature of $760^{\circ}\text{C}.$, which is reduced to 120°C on leaving the kiln. The dried weed, still retaining up to 25 per cent. of moisture, is next passed through incinerators of similar construction to the driers, but only 40 ft. long and 5 ft. in diameter—the flame being allowed to play directly into the cylinder. The charcoal-like product obtained at the discharge end, which contains about 35 per cent. of potash, is cooled and ground up, being then ready for sale to the manufacturers of compound fertilizers. The furnace gases and moisture are drawn from the discharge ends of the driers and incinerators by fans, and, as a certain amount of potash dust is carried over, the waste gases are led through a series of brick dust settling chambers, where most of this dust is deposited. According to Laucks [119] shredded waste wood is sometimes employed as a fuel for the driers.

The largest plant in the world for the treatment of wet seaweed was probably that of the Hercules Powder Co., near San Diego, California. It was erected in the first instance for the manufacture of acetone for munitions purposes, potash and other substances being by-products. The plant, which occupies an area of thirty acres, and cost about \$5,000,000 to construct, found employment for about 1,000 men. It is understood that since the cessation of the war, and the consequent decrease in demand for munitions products, the works have been practically idle.

During 1917, about 24,000 tons of weed was harvested per month. The cut weed is carried from the water to the harvester vessel by a series of moving screens which transfer it to macerators, whence it passes to the hold. The macerated weed is next conveyed by a suction pipe to a barge which takes the pulp ashore, whilst the harvester continues operations at sea. The pulp is transferred by suction to the fermentation tanks, of which there are 150 holding 50,000 gallons each. By carefully controlling the temperature of the tanks and securing aeration by means of compressed air, fermenta-

tion proceeds under control, the operation occupying from ten to fourteen days.

The decomposition of the cellulose and mucilaginous substances gives rise to the formation of acids of the acetic series, whilst the soluble mineral salts pass into solution in the water. At a certain stage in the fermentation, lime is added, the acetic, butyric, propionic acids being converted to their lime salts. When fermentation has proceeded far enough it is stopped by heating the mass to boiling point; the coarser insoluble matter is screened off and the liquid left for some days to clarify. The clear liquid, which contains about 4 to 5 per cent. of dissolved salts including about 1 per cent. of potash as chloride, is next treated in quadruple effect vacuum evaporators until the first crystalline product, known as *taffy*, separates out and is removed. On further evaporation, calcium acetate, containing a little potash, is obtained, and the liquid then is allowed to cool, when potassium chloride is obtained.

From the *taffy* is prepared on a large scale ethyl butyrate, ethyl propionate, methyl-ethyl ketone and other ketones now utilized as solvents.

The calcium acetate is used for the preparation of acetone by distillation, and the residue in the still, which contains potash and iodides, serves for the manufacture of iodine and 95 per cent. potassium chloride (nearly free from sulphate) [122]. Reliance cannot be placed upon estimated profits from the production of iodine from seaweed, as the world's demand is normally met by one-twelfth of the possible production from Chilean saltpetre, from which iodine can be produced at so low a cost as to be below competition [121].

So far the production of potash from seaweed has been small in comparison with the demand for potash fertilizers. The product has been chiefly used for chemical purposes on account of its high degree of purity [122].

It has been stated that algin has also been prepared from the insoluble matter remaining in the fermentation vats by extraction with sodium carbonate. Additional products made experimentally at the Hercules plant included valeric and caproic acids and ammonia [123].

According to R. K. Meade [124] the possibilities of the

commercial production of potash salts from kelp on a large scale are far from bright, since the production of 20 tons of potash involves handling about 1,500 tons of raw weed containing 1,350 tons of water. If this water were removed by rotary driers, about 38,000 gallons of oil would be required as fuel, an amount which under normal conditions would leave but little profit on the process. The cost of harvesting the weed alone appears to be prohibitive at present.

Further information on the American seaweeds is given by A. R. Merz [125]; D. M. Balch [126]; F. K. Cameron [127]; and by E. G. Parker and J. R. Lindmuth [128].

RAW SEAWEED AS A POTASH FERTILIZER

The use of fresh seaweed as a fertilizer has been the practice for many years along the coasts of Great Britain. The fertilizer is valued on account of its potash, nitrogen and organic matter contents, especially as the last named in many seaweeds is in a form which decomposes readily in the soil.

The potash, nitrogen and phosphoric acid contents of several marine plants common round the British Isles are shown in the following table, the results being expressed on the dried weed :

	Potash (K ₂ O).	Nitrogen (N).	Phosphoric acid (P ₂ O ₅).
	Per cent.	Per cent.	Per cent.
<i>Fucus</i> sp., Jersey	5.88	2.25	0.66
<i>Fucus ceranoides</i> , Devon	3.80	1.25	0.03
<i>Fucus nodosus</i> , Scotland	4.73	2.60	0.32
<i>Laminaria</i> sp., Scotland	6.84	2.57	0.80
<i>Fucus serratus</i> , Kent	3.70	2.33	0.05

On the south-west coast of Scotland, it is employed on many light soils, being much favoured for early potatoes, the quantity used for this purpose varying from 25 to 30 tons per acre. In Devon and Cornwall, for fertilizing potatoes and root crops, the weed is not usually applied in the fresh state, but is mixed with sand and allowed to rot before being employed.

The weeds chiefly used in this part of the country are *Fucus vesiculosus*, *F. serratus* and *Laminaria digitata*, whilst *Ulva lactuca* is occasionally employed.

In the Scilly Isles, seaweed constitutes the most important fertilizer, as much as 50 tons per acre often being used for potatoes. *F. serratus* is most used, whilst the *Laminaria* spp. are held to be of the least value.

In addition to the drift weed cast up by the tide, in Jersey cut weed from the rocks is largely used; the practice being to apply the fertilizer in the middle of September, at the rate of about 45 tons per acre.

In Thanet, the weed is often applied at the rate of 10 or 15 tons per acre over lucerne or sainfoin in the autumn and raked off in spring, just before the crop starts. It is also sometimes ploughed in before sowing market-garden crops.

Information on the fertilizing value of seaweed is given by J. Hendrick [129], by E. J. Russell [130], and by J. J. Skinner and A. M. Jackson [131].

WOOD ASH

As potash is necessary for the growth of plants, it is found, in varying amounts, in their ash. Prior to the middle of the last century, wood ash constituted the chief source of potassium carbonate, but the exploitation of the Stassfurt salt deposits led to a considerable decrease in the use of wood ash for this purpose. In certain localities, where large quantities of wood fuel are used or where much waste wood is produced, such as in lumber camps, the manufacture of potashes and pearl ash is still carried on. This is the case in certain parts of Canada, the United States, Russia and Spain. It is customary to use the term "pot-ashes" for the product obtained by calcination of wood and subsequent lixiviation and evaporation, whilst "pearl ash" is used to define the fairly high-grade potassium carbonate obtained therefrom.

The residues of all plants are not of equal value as sources of potash, as it has been found that those carrying large percentages of silica (such as the *Gramineæ*), or of phosphoric acid, yield little potassium carbonate. For this reason the

utilization of straw for the preparation of potash is not feasible.

Great variation is shown in the composition of the mineral matter from various portions of the same plant. As a general rule the proportion of ash is greater in the limbs and branches than in the inside wood, whilst the alkalies and phosphoric acid attain a maximum in the fruits and their envelopes.

The percentage of potash in the ash of a wood will naturally vary to some extent with the nature of the soil upon which it has been grown, but the following figures show the average contents of ash and of potash in certain plants in an air-dried condition.

*Percentages of Ash and Potash in Air-dried Plants **

—	Ash.	Potash in ash.	—	Ash.	Potash in ash.
	Per cent.	Per cent.		Per cent.	Per cent.
Ash wood . . .	1.22	6.06	Manuka wood (<i>Lep-</i>	—	1.66
Banana plant . . .	—	38.84	<i>tospermum</i> spp.) .	—	—
Banana skins . . .	18.0	62.5	Mallee wood (<i>Euca-</i>	—	2.42
Boxwood . . .	—	1.85	<i>lyptus</i> spp.) . . .	—	—
Bush flax (<i>Astelia</i>	—	23.27	Oak (post) wood . . .	0.77	21.92
<i>nervosa</i>) . . .	—	40	Oak (post) bark . . .	12.10	2.06
Bracken (see p. 104) .	6.0	6.49	Olive wood . . .	0.69	26.76
Sugar cane tops . . .	—	4.90	Peppermint wood . . .	—	4.06
Sugar cane trash . . .	—	13.3	Prickly pear . . .	1.2	9.48
Cardamon stem . . .	3.3	4.81	Red gum . . .	0.38	4.17
Cedar wood . . .	—	18.10	Red pine . . .	—	3.10
Chestnut wood . . .	0.16	29.11	Sage brush (p. 103) .	2.97	21.05
Coconut husk . . .	—	30.9	Sisal hemp . . .	—	8.00
Cotton seed . . .	3.78	23.4	Sunflower stalk and	—	49.6
Cotton seed hull . . .	2.4	11.4	leaves (p. 102) . . .	—	23.17
Elm wood . . .	2.55	20.2	Sycamore wood . . .	0.99	26.96
Grape marc . . .	11.6	1.48	Tobacco stems . . .	—	25
Kauri waste . . .	—	19.54	Water hyacinth . . .	—	17.04
Magnolia wood . . .	0.36	1.34	Wattle wood . . .	0.54	10.2
Mangrove (black) (<i>Rhi-</i>	—	—	Willow wood . . .	2.8	37.8
<i>sophora mucronata</i>)	—	—	Wormwood . . .	7.1	—

* Compiled chiefly from "Analyses of Fertilizers," *Queensland Agric. Jour.*, 1917, 7, 36; *Aschenanalysen*, by E. Wolff; Ref. [150] and analyses made at Imperial Institute.

The mean composition of ninety-seven commercial samples of unleached wood ashes as given by Grossman is shown in the following table :

—		Mean.	Maximum.	Minimum.
		Per cent.	Per cent.	Per cent.
Potash	K ₂ O . . .	5.5	10.2	2.5
Phosphoric anhydride	P ₂ O ₅ . . .	1.9	4.0	0.3
Lime	CaO . . .	34.3	50.9	18.0
Magnesia	MgO . . .	3.5	7.5	2.3
Insoluble matter	12.9	27.9	2.1
Moisture	12.0	28.6	0.7
Carbon dioxide, etc.	29.9	—	—

The examination of a number of samples of saw-mill waste ash, by C. T. Gingham [132] showed an average content of 6.73 per cent. of potash.

It will be noticed that wormwood (*Artemisia vulgaris*) contains a high percentage of potash, and in this connection it is interesting to note that large tracts of mountainous land in India are covered with various species of this genus, the preparation of pot-ashes from which has been recommended as a possible native industry [133].

It is evident from the above figures that large quantities of wood are necessary for the production of potassium carbonate in any quantity. Thus the production of one ton of anhydrous potassium carbonate from beech wood would require 452 tons of the wood, assuming that all the potash is recovered from the ash, an operation rarely possible on a commercial scale. The amount of ash yielded by this quantity of wood would be about 2.62 tons. The production of potash from wood can therefore only be carried out remuneratively in a locality where large quantities of waste wood are available or where much wood is used as fuel and the ashes can be easily collected. It has been suggested that much of the waste sawdust obtained in the woodworking industries might be utilized for this purpose if a cheap means of collection could be employed.

The following briefly describes the preparation of pot-ashes and pearl ash from wood (for further details see references [75], [134] and [135]).

The wood is burnt in pits, sheltered from the wind, the ashes are collected, spread upon stone slabs, and slightly moistened with water. In Canada and the United States

from 50 lb. to 80 lb. of slaked lime are added per 1,000 lb. of wood ash, in order to causticize the potassium carbonate, and liberate some of the base from potassium silicate. The damp ash is then packed in barrels, having false bottoms covered with straw, and hot water is poured over it. The liquor (over 19.8° Bé., specific gravity 1.16), which contains most of the soluble salts, is drawn off from time to time, and is afterwards concentrated by evaporation. Liquors of lower density are used for lixiviating further quantities of ash. The residue, still containing a fair amount of potash, is sometimes employed as a fertilizer.

A simple process for the economical leaching of wood ashes on the counter-current principle is described in reference [135].

The concentrated liquors obtained by leaching are evaporated to dryness in cast-iron pans fired from below, although pans fired from above would be more economical. There must be vigorous stirring during the latter part of evaporation, to prevent as much as possible the mass burning on to the pan. The mass of crude potash is then calcined in a reverberatory furnace below fusion point, organic matter being thereby removed and sulphides converted into sulphates.

To produce pearl ash, the crude pot-ashes are mixed with a little sawdust and recalcined. The product is dissolved in two parts of water, filtered from insoluble matter and allowed to cool. After a few days, the clear liquid is separated from the potassium sulphate and some chloride, which has deposited, and is then evaporated to dryness and again calcined. A still purer product is obtained by evaporating the final solution only to crystallization and then removing and calcining the deposited crystals.

The principal constituents of certain commercial brands of pot-ashes and pearl ash prepared from wood are shown in the table on the opposite page.

The greater proportion of the pot-ashes and pearl ash produced in Canada before the war was exported to the United Kingdom and used as a source of caustic potash. However, owing to the German caustic potash having fallen in price, the work proved unremunerative, which explains the decrease in the exports during the years immediately preceding the war. Moreover,

	Montreal pot-ashes.			Canadian pearl ash.		American pot-ashes.	
	Firsts.	Seconds.	Thirds.			1st quality.	2nd quality.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Potassium carbonate K_2CO_3	26.16	21.71	46.31	71.3	65.0	41.7	34.5
„ hydroxide KOH	36.50	30.63	6.14	—	—	49.6	29.6
„ sulphate K_2SO_4	10.40	9.18	20.53	14.3	21.0	4.0	15.0
„ chloride KCl	1.68	6.13	7.63	3.6	7.0	2.0	7.5
Sodium carbonate Na_2CO_3	2.84	8.52	17.81	2.3	4.0	1.4	3.0
Total available potash calculated as K_2CO_3	85.54	73.98	53.86	71.3	65.0	106.4	77.9

it appears (from a report furnished, in 1915, to the Imperial Institute by the Forestry Branch, Department of the Interior, Canada) that much of the wood cut in Canada is soft wood, containing a much lower percentage of potash than the harder varieties formerly cut, which has also contributed towards the decrease.

The conclusion arrived at in the report with regard to the production of potash from wood ashes in Canada, is that it is not commercially feasible to revive the potash industry as practised in Canada twenty-five years ago, and that, in most cases, the only use for the ash from saw-mill burners is for the farmers in the locality to apply it directly to their land.

Large accumulations of wood ash often occur where wood is used as a fuel. This is particularly the case on the railways of Kenya Colony. Samples of wattle, chestnut and olive wood ashes from this source have recently been examined at the Imperial Institute with the following results :

	Chestnut wood ash.	Wattle wood ash.	Olive wood ash.
	Per cent.	Per cent.	Per cent.
Potash soluble in water K_2O	5.38	6.98	2.13
„ insoluble in water K_2O	0.26	0.78	0.04
Soda soluble in water Na_2O	1.34	1.24	0.66
„ insoluble in water Na_2O	1.71	0.80	1.32
Crude potashes recoverable per ton of ash	228	291	102

It appears probable that the above ashes had been partly leached by exposure to the weather, as the amount of potash

in the wattle and olive wood compares unfavourably with that found in other specimens of ash from these woods from the same colony examined in the Scientific and Technical Research Department of the Imperial Institute.

In Argentina many large industrial plants employ Quebracho wood as fuel, and it has been proposed to utilize the ashes for the manufacture of potash.

Potash is produced in the Abdali and Fadhli districts of Aden, Arabia, by burning the Aden balsam with wood fuel in shallow pits. The crude ash is sent to Aden, and exported to Bombay.

VEGETABLE WASTE

Hedge Clippings

It has been suggested that much of the vegetable waste of the farm and garden might be burnt and the ashes used as a potash fertilizer. Experiments carried out at Rothamsted [136] have shown that the ash of hedge cleanings from three fields contained on an average 10.9 per cent. of potash. The ashes must be protected from the rain while cooling, then mixed with superphosphates of lime and applied at once to the soil. The quantity of ash may vary from 5 to 20 lb. per 100 yards of hedge trimmings.

Sunflower Stalks

The ashes from the stalks of sunflowers are the main source of potash in Russia, and the industry is important [153]. The sunflowers are grown on waste land, mostly in Northern Caucasia and in the Saratov region. There were twenty-eight potash factories in the former district in 1912, controlled by a Moscow syndicate. The total Russian production in 1911 was 13,232 short tons.

In the period 1915-17 the average annual production in Northern Caucasia was from 15 to 17 thousand short tons of 88 to 90 per cent. of potassium carbonate, that of the Saratov region being from 2,500 to 3,500 tons of 78 to 80 per cent. of potassium carbonate. In 1918 and 1920 it was estimated that the United States imported 5,000 and 600 short tons respectively of Russian potassium carbonate.

Sunflower stalk ash has recently been prepared from plants grown in Rhodesia, and the material was submitted to examination at the Imperial Institute with the following results :

		Soluble in water. Per cent.	Insoluble in water. Per cent.
Potash	K ₂ O . . .	36.73	0.22
Soda	Na ₂ O . . .	1.66	0.82
Lime	CaO . . .	nil	18.90
Magnesia	MgO . . .	nil	—
Sulphuric anhydride	SO ₃ . . .	0.73	—
Chlorine	Cl . . .	2.48	—
Phosphoric anhydride	P ₂ O ₅ . . .	nil	0.69

It appears that the ash of sunflowers grown in Rhodesia is subject to somewhat wide variation in potash content, as the ash of a previous sample of stalks contained 49.6 per cent. of potash.

The composition of the soluble matter in Rhodesian sunflower ash and that of Russian pot ash is shown in the following table :

		Rhodesian. Per cent.	Russian. Per cent.
Potassium carbonate	K ₂ CO ₃ . . .	{ 83.4* }	83.80
„ hydroxide	KOH . . .		4.72
„ sulphate	K ₂ SO ₄ . . .		2.7
„ chloride	KCl . . .		9.0
„ phosphate	K ₂ HPO ₄ . . .		—
Sodium carbonate	Na ₂ CO ₃ . . .	4.9	—

* Calculated as K₂CO₃.

Tobacco Plant Stems

These have been used to a small extent in the United States for the production of high-grade potassium chloride, but the material seems to be more frequently utilized as a component of mixed fertilizers. The stems, which contain about 20 per cent. of moisture, are dried until this is reduced to about 2 to 4 per cent. and then finely ground. They then contain about 5 per cent. of potash, and when added to a mixture of artificial fertilizers act as both “ drier ” and “ filler.”

Sagebrush (Artemisia sp.)

This shrub contains variable amounts of potash—in one case as much as 21.05 per cent.—and a volatile oil is also obtainable

from it. The plant grows wild in several of the Western States of America, and various attempts have been made to utilize it, but none of the projects seems to have been a commercial success [3/p. 156].

Water Hyacinth (Eichornia crassipes)

In Burma, Bengal, and other parts of India, this plant has become a serious pest, and steps have been taken for its eradication. Its value as a fertilizer has recently been discussed by R. S. Finlow and K. McLean [137]. The dried plant, which constitutes about one twentieth of the wet material, contains about 8 per cent. of potash (K_2O), whilst the ash has an average of 25 per cent. potash, but the quantity varies with the conditions of growth and nature of the soil as shown by the following analyses :

		I.	II.
		Per cent.	Per cent.
Potash	K_2O	34.15	11.36
Phosphoric anhydride	P_2O_5	8.20	1.41
Lime	CaO	8.43	7.79
Chlorine	Cl	20.37	5.66
Silica	SiO_2	20.72	49.43

Analysis No. I was made on ash prepared from a well grown plant from the Dacca khal, whilst No. II represents the ash of a stunted plant grown on red soil at Mirpur (*see* [178]).

It was stated in June 1917 that, so far, about 170 tons of water hyacinth ash, representing 17,000 tons of the green plant, had been sold in Calcutta and Dacca.

Prickly Pear

The eradication of this pest has received considerable attention in Australia, and the recovery of potash by burning the dried plant has been attempted. It was reported in 1917 that the process was not yet a commercial success [138].

Bracken

Bracken has received some attention, particularly in the United Kingdom, as a possible source of potash. The plant is stated to have been used many years ago in certain parts

of Wales for the production of a crude form of soda-ash used for making soap and glass. The composition of bracken at various stages of its growth has been investigated by R. A. Berry [139], and by R. A. Berry, G. W. Robinson and E. J. Russell [141], who found that the young plant gave an ash containing about 50 per cent. of potash, whilst the mature material gave a larger quantity of ash containing a smaller percentage of potash. When the dead bracken has lain exposed to the weather the content of potash may be as low as 2 per cent. Bracken grown on sandy soils gave considerably less potash than that grown on loams. In most cases the quantity of water-soluble potash was about 90 per cent. of the total potash, but in some cases this fell to as low as 50 per cent.

The variation in yield of ash and potash with the season is shown in the following table, the bracken under consideration being obtained from Dundonald Glen in Ayrshire :

Monthly sampling, 1916.	Dry matter calculated on fresh bracken.	Potash in fresh bracken.	Ash in dry matter.	Potash in ash.	Ash per acre.
	Per cent.	Per cent.	Per cent.	Per cent.	lb.
May . . .	8.0	0.42	9.4	56	41
June . . .	15.5	0.59	7.2	53	287
July . . .	21.5	0.65	6.4	47	556
August . . .	26.1	0.70	6.3	42	678
September . . .	28.4	0.64	6.1	37	601
October . . .	73.9	0.56	3.5	21	186

From estimates made in 1918 it would appear that the cost of preparing the ash would now more than equal the market value of the product.

When the eradication of bracken is desired, it should be gathered when approaching maturity, indicated by the slight yellowing of the fronds; after air-drying, it should be carefully burnt and the ash protected from the weather.

B. C. Aston [140] gives calculated values from £24 5s. to £16 5s. per ton of ash from mature plants grown in New Zealand (assuming potash to be worth 12s. 6d. per unit). Preliminary results indicated that the yield of ash per acre would be considerably larger than that obtainable in Scotland.

OTHER VEGETABLE SOURCES OF POTASH

Kegu or *Kighr* salt is prepared by the natives in certain districts around Lake Chad from the ash of the "kegu" tree, which is stated to be the *Salvadora persica*.

It has been stated, however, that the *Kighr* salt of Bornu Province is obtained by burning the roots and stems of a climbing bush, possibly the *Capparis Sodada*.

Numerous samples of the salt have been examined in the Scientific and Technical Department of the Imperial Institute, and found to contain considerable quantities of potassium chloride, as shown by the analyses given below.

In times of scarcity a salt is prepared from the ash of three grasses, growing around Lake Chad, whose local names are *Kajiji*, *Kalatsilim* and *Kamgabi*. This salt, which is sometimes known as *Manda Karia*, appears to be of variable composition, as indicated by the analyses made at the Imperial Institute and shown in the following table :

	1.	2.	3.	4.	5.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Potassium chloride KCl .	57.88	28.76	35.46	2.54	8.98
Sodium chloride NaCl .	26.83	67.60	37.46	50.07	83.78
„ sulphate Na ₂ SO ₄	0.67	1.42	21.51	29.39	0.90
„ carbonate Na ₂ CO ₃	0.22	—	1.95	4.99	—
„ bicarbonate NaHCO ₃	—	—	1.52	—	—
„ phoshate Na ₂ HPO ₄	—	—	0.11	5.48	—
Calcium sulphate CaSO ₄	—	1.48	—	—	—
„ chloride CaCl ₂ .	—	—	—	—	1.73
Magnesium chloride MgCl ₂ .	—	—	—	—	0.07
Boric anhydride B ₂ O ₅ .	—	—	—	1.36	—
Insoluble matter	11.89	0.36	0.48	0.58	2.14
Moisture	2.11	0.37	1.65	5.23	1.92

1. *Kighr* salt made at Bosso, French Territory.
2. *Kighr* salt made in Chad district, Bornu Province, Nigeria.
3. *Manda Karia* made at Ngornu, Nigeria.
4. *Manda Karia* from Bornu Province.
5. *Kighr* salt from north-west of the River Komadugu Waube, Bornu Province, Nigeria.

CHAPTER X

RESIDUES FROM BEET-SUGAR MANUFACTURE

THE sugar-beet contains an average of 0.3 to 0.5 per cent. of potash (K_2O), present partly as nitrate and partly in combination with organic acids. The crystallized sugar from the beet contains little potash, but the molasses may contain up to 5 per cent.

According to H. E. Zitkowski [142] about 10 per cent. of the total potash in the sugar-beet crop, grown in the United States, is returned to the land in waste pulp, whilst about 90 per cent. passes into the molasses, about 40 per cent. of which is treated for the recovery of sugar. In 1916, of the potash present in the molasses thus treated, 70 per cent. was discharged into streams and lost, so that about 28 per cent. of the total potash present in the crop was wasted at the molasses treatment works alone.

In general, there are two processes for utilizing the molasses : (1) for the production of alcohol ; (2) for obtaining further quantities of sugar by the strontia, lime or " osmose " processes. In the first case, the molasses is diluted with water, acidulated with sulphuric acid and fermented with yeast ; after distilling off the spirit thus produced, the residue (vinasse, slop, schlempe or dunder), which contains probably between 1.0 and 1.5 per cent. of potash, may be used directly as a fertilizer, or be first treated for the potash salts which it contains.

In New Orleans, in 1916, a distillery was treating about 250,000 gallons per day, and producing about 3,000 lb. of potash (K_2O) chiefly in the form of chlorides. The liquid is first evaporated until it contains 50 per cent. of moisture and 3 per cent. of potash. The residue is then fed into a rotary kiln in which the material is burnt spontaneously, after the ignition has been started by oil fuel. The ash obtained

is leached with water, and its potash recovered from the solution by evaporation and crystallization.

It is said that in 1918 the potash recovered at the molasses plants in the United States cost nearly \$2 per unit, but it was anticipated that in a few years' time the cost would compare favourably with that of imported German potash.

During the years 1916-20 the quantities of potash (K_2O) contained in the salts recovered at factories in the United States, treating distillery waste and waste water from the Steffens sugar process, were respectively as follows: 1,845, 3,215, 4,841, 6,420 and 6,647 short tons. The output in 1920 was obtained from 14 factories as compared with 16 and 15 in 1918 and 1919 respectively.

J. Ginsberg [145] gives details of a process employed some years ago at the Raab spirit factory, Hungary. The neutralized waste (120-140 metric tons per day) was passed through three evaporators, the first being steam-heated, and with 180 square metres of heating surface. A partial vacuum was maintained in the second and third evaporators, the temperatures being kept at between 80° and 90° C. and between 60° and 70° C. respectively. The liquid (40° Bé.) leaving the last pan was carbonized in two ovens without additional fuel. The smouldering mass, discharged into small trucks, was burnt to an ash, which varied in percentage composition as follows: potassium carbonate (K_2CO_3), 56-58; potassium sulphate (K_2SO_4), 8-10; potassium chloride (KCl), 6-7; potassium phosphate (K_2HPO_4), 0.4-0.6; sodium carbonate (Na_2CO_3), 10-12; sodium sulphate (Na_2SO_4), 0.3-0.4; insoluble matter, 10-11; organic matter, 1-1.5; water, 0.5-5.4. The ash was ground in ball mills and then lixiviated with hot dilute lye. On evaporating the extract to 46° - 47° Bé. in a vacuum pan, potassium sulphate crystallized out, and on cooling the solution to 25° - 30° C. a crop of potassium chloride was obtained. The mother liquor was then concentrated to 50° - 53° Bé., and then gave a deposit of double carbonate of potassium and sodium mainly. On further cooling, there was obtained successively crops of impure potassium chloride and the double carbonate.

Other processes have been used, some involving the

treatment of the vinasse residue in cast-iron retorts so as to recover such volatile products as ammonia, etc. Factories in Germany, employing the Bueb process of destructive distillation, are said to have produced annually from the waste of molasses treatment processes about 5,000 tons each of potassium cyanide and ammonium sulphate [142].

Certain distilleries in Italy sell a product known as "salino potassico," which is stated to contain 47.2 per cent. of potash (K_2O).

With the "osmose" process for recovering sugar from molasses the liquors obtained are too weak to repay evaporation. In the lime process the dilute waste water, containing 0.2-0.5 per cent. of free lime, is treated with carbonic acid to get rid of the lime, and the liquid, after filtration, has the following percentage composition: Moisture, 97; sugar, 0.30; nitrogen, 0.16; potash, 0.35; and organic matter, 1.70. It can be concentrated in multiple-effect evaporators until it contains 50 to 55 per cent. of solid matter, when it begins to "salt out." If the operation is continued in a vacuum drum evaporator, the material can be completely dried, and will then contain 10 to 12 per cent. of potash (K_2O) and 5 per cent. nitrogen.

Before the war potash was recovered at a number of beet-sugar refineries in Europe, particularly in Belgium and Northern France, and, during the war, the recovery was carried out at Choisy le Roi, Seine [143]. During 1915, residual liquors from the treatment of molasses by the barium process were evaporated at the works of the Dominion Sugar Co. of Ontario. The concentrated waste liquor, containing 11 or 12 per cent. potash and 4 per cent. nitrogen, was sold to fertilizer manufacturers [144]. It is said that Germany exported 1,322, 3,372 and 933 tons of crude potash recovered from beet-sugar residues during 1911, 1912 and 1913 respectively [146].

CHAPTER XI

ANIMAL SOURCES OF POTASH

WOOL WASHINGS

THE material known as wool yolk, which is removed to the extent of from 15 to 70 per cent. by washing raw wool, consists of wool-grease, sand and dried sweat or *suint*. The last consists of potash combined with certain fatty acids, and can be removed from raw wool, prior to scouring, by treating it in water. The matter soluble in water usually amounts to 14 to 18 per cent., and contains potash equivalent to 2 to 7 per cent. of potassium carbonate (calculated on the raw wool), the amount depending largely on the breed of the sheep.

The recovery of the potash is not remunerative unless conducted on a large scale, and hence the three constituents of wool yolk are often removed together in the process of scouring and allowed to go to waste. It is reported that in the United States the wool washings from certain large slaughter houses are run through peat, which absorbs the potash, and the material thus obtained is used as a filler for certain complete fertilizers.

In Belgium, France and Germany, the wool, before scouring, is treated with cold water either in a mechanical washer or in a series of tanks, the last washings from one batch of wool being used for the first treatment of the next (i.e. a counter-current system is used). The brown washings (sp. gr. about 1.12) are evaporated nearly to dryness in iron pans in a Porian type of evaporator, and the pasty mass is calcined in a reverberatory furnace, or destructively distilled in clay gas retorts. In the latter case, the nitrogen in the grease is recovered, as ammonia and cyanogen, and the combustible gases evolved are used for heating purposes. The carbonaceous

residue, which contains from 58 to 65 per cent. of potassium carbonate, is crushed and then lixiviated with water in iron or wooden vats. The clear liquid is evaporated to crystallization, and successive crops of potassium chloride and carbonates are obtained.

It is stated that in the suint obtained from sheep bred inland, the ratio of potash to soda is 40 to 1, whilst in that from coast sheep the ratio is about 7 to 1. Analyses of potassium carbonate prepared from suint show from 80.57 to 91.20 per cent. of potassium carbonate, other salts present being potassium sulphate, potassium chloride and sodium carbonate.

Formerly the fatty solids in wool scouring waste liquors were recovered by precipitation with sulphuric acid or acid sodium sulphate, and the potash was lost in the waste liquor. The Smith-Leach process (British) was designed to recover both potash and wool-grease from scouring liquors. Sand is first mainly removed in settling tanks, the liquors passing on to multiple-effect evaporators, where the volume of the solution is reduced to one-tenth. The hot liquor is then passed through a centrifuge, and so caused to separate into (1) an outer layer of sand; (2) a middle layer of soap solution which carries the potash; and (3) an inner layer of wool-grease. The last is removed continuously by means of a skimming pipe, and, after further purification, is ready for sale. The potash and soap solution is further evaporated to dryness, and then incinerated, crude potassium carbonate being produced. The process has been used at certain mills in Bradford. According to A. W. G. Wilson [147] 55,000 gallons of suds will by the process yield 2 tons of wool-fat and 1 ton of potassium carbonate. The pre-war cost of a plant capable of dealing with 60,000 gallons of waste liquor per week was estimated at about £4,500.

The cost of evaporation is said to be reduced to one-fourth in the process described by E. V. Chambers [148]. Greasy wool is passed through a scouring bowl until the solution is too dirty for further use. The liquor is then run to settling-tanks and thence through a high-speed centrifugal machine, at the rate of 250 gallons per hour, where separation of sand,

liquor and wool-grease takes place as in the Smith-Leach process. The middle liquid is sent back for use in the scouring bowls until again saturated with grease, when the centrifugal treatment is repeated. These operations are carried on for about four or five cycles, when the liquor, which will then contain from 6 to 8 per cent. of potash, is incinerated in a rotary apparatus.

The working costs in 1916 for treating 45,000 gallons of scouring liquor per week amounted to £20 6s., and the value of the product obtained and material saved per week amounted to £46 12s., leaving a net annual estimated profit of £1,315.

According to R. S. Weston [149] good results are obtained by passing the hot liquor from the centrifuge through a Cardem evaporator, especially if waste flue gases are available for heating purposes.

D. C. Winterbottom [150] estimates that the total wool scoured in Australia would yield 2,812 tons of potassium carbonate per annum. At the present time both potash and wool-fat (lanolin, etc.) go to waste, and it has been suggested that portions of the wool richest in potash and fat might be profitably treated. Experiments made in South Australia showed that fleece wools when washed in cold water gave from 2 to 3 per cent. of pot-ashes, whilst locks and stained pieces gave from 4.5 to 6.25 per cent. of pot-ashes. The pot-ashes gave from 52.9 to 58.9 per cent. potash (K_2O).

Winterbottom (loc. cit.) estimates that a plant for treating 3,000 tons of greasy wool per annum would cost about £1,700. Putting working cost at £1,504, and the revenue (from 157½ tons of potassium carbonate at £15 per ton) at £2,367, an estimated profit of £863 would be left.

The annual production of potash salts from wool before the war was estimated to be equivalent to from 5,000 to 10,000 tons of potash. The quantities of crude wool yolk ash exported from Germany in 1911, 1912 and 1913 were 14,467, 12,875 and 16,013 tons respectively [146/p. 1100].

KARROO ASH

Sheep dung is used to a large extent as fuel in the Karroo districts of Cape Province and in the Orange Free State. The

ash remaining after ignition has been given the name of Karroo ash, and it has been stated by B. de C. Marchand [115/p. 1122] that fully nine-tenths of the potash in the mixed fertilizers on the South African market in 1918 was obtained from this source. The ash is of varied composition, but contains, on the average—potash, 10 per cent. ; lime, 15.69 per cent. ; and phosphoric anhydride, 2.55 per cent.

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