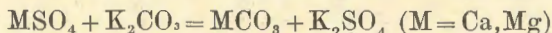


The Recovery of Potassium Carbonate from Wool Scouring Liquor and the Conversion of the Recovered Potassium Carbonate to Commercial Potassium Sulphate, using Naturally Occurring Gypsum as Sulphate Source.

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IN studying ways and means of converting, on a commercial basis, an alkali carbonate such as potassium carbonate to the corresponding alkali sulphate, one should bear in mind that the success of the conversion should be studied from the viewpoint of the efficiency of the cation exchange and not in terms of total potassium. The presence of potassium should be regarded as being merely incidental. Furthermore it has been found in the present study, contrary to analytical figures for wool suint from other parts of the world, that South African scouring liquors contain sulphate. In all probability the sulphate is contained in the scouring liquor as potassium sulphate. If potassium sulphate is not normally excreted through the skin of the sheep its presence in wool suint will naturally range from mere traces to considerable quantities.

The presence of potassium sulphate in wool suint may feasibly be ascribed to (a) a sulphate containing ground and a sulphate containing burned veld ash contamination of the wool; (b) the dipping of sheep in sulphate-carrying waters. Under these conditions the reaction:—



will gradually proceed in the wool suint. The presence of potassium chloride in wool suint has been known for a long time.

On account of the reasons stated above the problem was tackled by establishing in the first instance the initial active carbonate and sulphate content of the ash obtained by the destructive combustion of wool scouring liquor concentrate.

Analysis of ash.

- 34.37 per cent. active carbonate.
- = 79.16 per cent. in terms of potassium carbonate.
- 1.795 per cent. active sulphate.
- = 3.258 per cent. in terms of potassium sulphate.
- 3.505 per cent. active chloride.
- = 7.370 in terms of potassium chloride.

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Analysis of gypsum.

45.81 per cent. available SO₄ (conversion by Na₂CO₃).

44.34 per cent. available SO₄ (conversion by K₂CO₃).

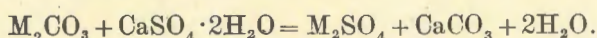
45.58 per cent. available SO₄ (conversion by (NH₄)₂CO₃).

Average = 81.14 per cent. CaSO₄·2H₂O.

Acid insoluble residue = 16.05 per cent. (sand).

EXPERIMENT A.

The conversion efficiency of carbonate to sulphate was studied in solutions obtained by the leaching of concentrated scouring liquor ash. The solutions adopted in this study contained an active carbonate concentration of 0.143 per cent. to 3.56 per cent. in terms of carbonate. By working from the equation:—



the stoichiometric quantity of powdered gypsum was added to each specific solution, the mixtures gently boiled for 30 minutes. (Tests were run in 250 ml. volumes.) After the solutions had been allowed to cool it was filtered, washed and the filtrate made up to standard volume. The sulphate, residual calcium and carbonate were determined in aliquots from the unit volume. The sulphate was determined gravimetrically, the calcium volumetrically by permanganate titration and the residual free carbonate by an accurate two-stage titration. In this way the efficiency of the cation exchange was checked from three sides.

The results are tabulated in Table 1.

TABLE 1.

A.	B.	C.	D.	E.	F.	G.	H.	I.	J.
1.0347	1.257	0.0452	8.30	2.30	1.3292	1.284	0.330	0.356	92.7
3.0235	3.671	0.1320	29.90	2.90	3.8220	3.690	0.949	1.040	91.2
6.0435	7.340	0.2639	68.80	1.75	7.5179	7.254	1.865	2.077	89.8
9.0051	10.930	0.3931	98.90	3.40	11.2530	10.860	2.791	3.094	90.2
11.9824	14.550	0.5232	145.5	2.70	14.8132	14.290	3.673	4.118	89.2
25.8500	31.390	1.1291	376.4	2.10	30.5390	29.411	7.560	8.710	86.8

A = Weight of ash per 250 ml.

B = 81.14% Gypsum equivalent of A.

C = BaSO₄ equivalent of the initial sulphate content.

D = Residual free carbonate in ml. O.I.N.

E = Residual free calcium in ml. O.I.N.

F = Total weight of BaSO₄.

G = BaSO₄ equivalent of potassium sulphate formed by cation exchange.

H = CO₃ equivalent of potassium sulphate formed by cation exchange.

I = Available CO₃.

J = Percentage conversion of carbonate to sulphate.

The conversion percentages arrived at in Table 1 are not absolute, as the BaSO_4 equivalent of the residual calcium in column E was not allowed for. However, this amount is almost entirely negligible.

EXPERIMENT B.

The experiment carried out in A was repeated on a further 250 ml. aliquot of the original leach. Gypsum was now added in an excess of 100 per cent. over and above the stoichiometric equivalent.

This large excess of gypsum was adopted in order to study the solubility of the excess gypsum in solutions with a progressive increase in potassium sulphate concentration. The results are tabulated in Table 2.

TABLE 2.

A.	B.	C.	D.	E.	F.	G.	H.	I.	J.	K.
1.0347	2.514	3.20	0.1531	1.8342	0.447	1.342	0.345	0.356	0.0452	96.92
3.0235	7.342	1.80	0.2183	4.7930	0.6368	4.023	1.034	1.040	0.1320	99.42
6.0435	14.680	0.25	0.3119	9.2372	0.9101	8.063	2.084	2.077	0.2639	100.3
9.0051	21.860	5.5	0.3839	13.4830	1.120	11.970	3.076	3.094	0.3931	99.19
11.982	29.120	0.34	0.4397	16.9732	1.283	16.167	4.157	4.118	0.5232	101.1
25.850	62.780	37.5	0.4793	35.947	1.398	33.420	8.592	8.710	1.1291	98.64

A = Weight of ash per 250 ml. volumes.

B = 81.14% Gypsum equivalent + 100% excess.

C = Residual free carbonate in ml. O.I.N.

D = Residual calcium in grams per 1,000 ml.

E = Total weight of BaSO_4 .

F = BaSO_4 equivalent of the residual calcium.

G = BaSO_4 equivalent of the potassium sulphate formed by cation exchange.

H = CO_2 equivalent of the potassium sulphate formed by cation exchange.

I = Available CO_2 .

J = BaSO_4 equivalent of the initial sulphate content.

K = Percentage conversion of carbonate to sulphate.

EXPERIMENT C.

Scouring Liquor Concentrate.

Scouring liquor was concentrated, evaporating 4 volumes of water per every initial 5 volumes of liquor. The liquor contains at this stage 2.649 grams of available carbonate per 100 grams of solution and a sulphate content of 0.208 per cent. in terms of sulphate.

The liquor was mixed with (a) the equivalent amount of powdered gypsum, (b) gypsum in 10 per cent. excess of the theoretical amount, and (c) gypsum in a 100 per cent. excess.

The mixtures were heated past the frothing stage, gradually combusted and finally ashed at dull red heat allowing sufficient air contact.

The results for the conversion of carbonate to sulphate are tabulated in Table 3.

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TABLE 3.

A.	B.	C.	D.	E.	F.	G.	H.	I.	J.	K.
23.4375	2.196	2.1515	.0464	40.9	.1185	0.124	1.909	.4909	.6209	79.1
20.707	2.134	2.5000	.1120	5.1	.1047	0.327	2.067	.5325	.5488	97.5
22.581	4.230	3.3020	.3020	1.2	.1142	0.881	2.308	.5933	.5981	99.2

- A = Weight of liquor.
 B = Weight of gypsum.
 C = Total weight BaSO₄.
 D = Residual Ca in grams per 1,000 ml.
 E = Residual CO₃ in ml. O.I.N.
 F = BaSO₄ equivalent of sulphate initially present.
 G = BaSO₄ equivalent of the residual calcium.
 H = BaSO₄ equivalent of potassium sulphate formed by cation exchange.
 I = CO₃ equivalent of potassium sulphate formed by cation exchange.
 J = Available CO₃.
 K = Percentage conversion of carbonate to sulphate.

EXPERIMENT D.

Centrifuged (Middle Portion) of the Concentrated Scouring Liquor.

The concentrated scouring liquor as used in Experiment C was centrifuged by Mr. Rossouw at approximately 4,000 r.p.m. for 60 minutes. The middle layer was used in this experiment for the recovery of potassium. This layer contained an available carbonate concentration of 2.826 grams CO₃ per 100 grams liquor and a sulphate content of 0.221 per cent. on a weight basis.

This middle layer should naturally be higher in both carbonate and sulphate content than the initial total fraction (see Experiment C) as the middle layer lost a considerable amount of fat and semi-colloidal material. The experiment as described under C was carried out on this middle fraction. The results are tabulated in Table 4.

TABLE 4.

A.	B.	C.	D.	E.	F.	G.	H.	I.	J.	K.
19.8042	1.979	1.9790	.0314	31.7	0.1064	0.0916	1.781	0.4580	.5595	81.84
18.9518	2.083	2.4235	.0929	2.2	0.1018	0.2707	2.051	0.5274	.5356	98.5

- A' = Weight of liquor.
 B = Weight of gypsum.
 C = Total weight of BaSO₄.
 D = Residual calcium in grams per 1,000 ml.
 E = Residual carbonate in ml. O.I.N.
 F = BaSO₄ equivalent of sulphate initially present.
 G = BaSO₄ equivalent of the residual calcium.
 H = BaSO₄ equivalent K₂SO₄ formed by cation exchange.
 I = Available CO₃.
 J = Available CO₃.
 K = Percentage conversion of carbonate to sulphate.

EXPERIMENT E.

Cold Scouring.

The scouring of wool with cold water was carried out by Mr. Rossouw. The scouring liquor showed an available carbonate content of 0.8056 grams CO_3 per 100 grams liquor and a sulphate content of 0.0554 grams SO_4 per 100 grams liquor.

The liquor was treated with (a) the stoichiometric equivalent of gypsum, (b) the equivalent of gypsum + 10 per cent. excess and (c) the equivalent of gypsum + 100 per cent. excess.

The mixtures were carefully heated past the frothing stage, combusted and finally ashed at dull red heat. The results for the conversion of carbonate to sulphate are tabulated in Table 5.

TABLE 5.

A.	B.	C.	D.	E.	F.	G.	H.	L.	J.	K.
500	15.67	12.6708	0.028	310.5	0.6491	0.0817	11.9400	3.078	4.028	76.4
500	17.237	16.1790	0.240	68.9	0.6491	0.7001	14.8298	3.813	4.028	94.65
500	31.34	17.0938	0.465	49.7	0.6491	1.355	15.1897	3.879	4.028	96.3

A = Weight liquor.

B = Weight gypsum.

C = Total weight BaSO_4 .

D = Residual Ca in grams per 1,000 ml.

E = Residual CO_3 in ml. O.I.N.

F = BaSO_4 equivalent of initial sulphate.

G = BaSO_4 equivalent of residual calcium.

H = BaSO_4 equivalent of K_2SO_4 formed by cation exchange.

I = CO_3 equivalent of K_2SO_4 formed by cation exchange.

J = Available CO_3 .

K = Percentage conversion of carbonate to sulphate.

DISCUSSION.

From the analytical data obtained in the various experiments it is evident that the quantitative conversion of potassium carbonate *ex* wool scouring liquor to potassium sulphate may readily be brought about on a commercial scale by a simple cation exchange reaction using natural gypsum as a source of available sulphate.

Low conversion percentages are encountered in cases where the gypsum is added in quantities just sufficient to allow a stoichiometric reaction. This may be accounted for by the possible development of a time reaction in dilute aqueous solutions or in the case of the concentrated masses it may be due to an insufficient intimate contact between the carbonate and the particles of gypsum. As soon as gypsum is added in excess the carbonate to sulphate conversion becomes quantitative. In some cases a large excess (100 per cent.) of gypsum was employed in order to study the solubility of the free gypsum in varying concentrations of potassium sulphate.

The values given for the residual calcium (Table 2, column D) is not a true reflection of the solubility of gypsum in solutions of potassium sulphate as tests were run in 250 ml. volumes which were filtered and made up to

500 ml. with cold water. Thus the figures contained in Table 2, column D is a reflection partially of the true solubility of gypsum in potassium sulphate and partially of the leaching effect of the added cold water. Actually the solubility of gypsum is decreased by potassium sulphate. The cation exchange carbonate-sulphate takes place in—

- (a) aqueous solutions of wool scouring ash;
- (b) concentrated scouring liquors with all the fat present or partially removed;
- (c) scouring liquor obtained from the cold steeping of wool;
- (d) an intimate mixture of wool scouring liquor ash and gypsum, if the mixture is heated to dull red heat.

Naturally in practice the approach to the problem of the recovery of potassium as potassium sulphate *ex* wool suint. would be from the most economic angle. In this connection a few points should be carefully considered. If gypsum is added to—

- (a) natural scouring liquor;
- (b) concentrated scouring liquor with or without the partial removal of fat;
- (c) mixed with the correct weight of ash, and the process of recovery culminates in ashing, great care should be exercised not to exceed the transition temperature of calcium carbonate. If the transition temperature of calcium carbonate is exceeded it is readily conceivable that the final solution containing the potassium sulphate may be contaminated with free potassium hydroxide.

If in practice a cycle process is applied, i.e., allowing an excess of carbonate with the view of using the carbonate-containing mother liquor to facilitate the scouring of wool then the presence of free potassium hydroxide would be disastrous. The presence of free hydroxyl ions in the final solution is indicated if in the two-stage acid titration the cold and hot titrations do not correspond.

It would appear that the most efficient procedure for the conversion of potassium carbonate from scouring liquor to potassium sulphate would briefly be as follows—

- (a) a triple effect evaporation of the scouring liquor with the removal of approximately four volumes of water per every five volumes of initial liquor;
- (b) the removal of fat by mechanical means;
- (c) further evaporation of the middle centrifuge layer, combustion and ashing with sufficient air contact. The ashing temperature should not exceed the volatilization temperature of potassium chloride;
- (d) the ash is leached with water, controlling the ash-water system, such that the gypsum conversion of the potassium carbonate results in a solution containing potassium sulphate in excess of the cold saturation point of potassium sulphate, i.e., crystallization would be spontaneous. The residual carbon in the ash together with the sand residue of the gypsum serve as an excellent filter aid.