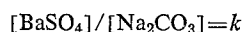1

The present invention is concerned with a process for
the continuous production of barium carbonate from
barium sulfate.

In the preparation of the caustic solution for alkali
chloride electrolyses, considerable quantities of barium
sulfate are formed. So far no economic method has
existed for the return of this sulfate to the process.

With the conventional technical processes for the pro-
duction of barium carbonate, finely ground heavy spar
is reduced in a rotary furnace with carbon to barium
sulfate which is then reacted in aqueous medium with
carbon dioxide.

It is known that barium sulfate can be decomposed
with aqueous soda solution if sodium carbonate is pres-
ent in excess. Based on these facts, several technical
processes for the production of barium carbonate have
been developed, but they all have the disadvantage of
needing large reaction vessels and containers since the
operation is performed by batches. The process is eco-
nomically inefficient on account of this intermittent oper-
ation.

In an investigation of the decomposition reaction be-
tween barium sulfate and sodium carbonate, it has now
been found that the equilibrium corresponding to the
formula

$$[BaSO_4]/[Na_2CO_3]=k$$

where k is a constant highly dependent on temperature,
is rapidly adjusted to the decomposition side, especially
when the decomposition is carried out at temperatures of
100° C. and higher. The reaction is hindered in the re-
verse direction.

A process for the production of barium carbonate by
reacting the barium sulfate under pressure with excess
dilute sodium carbonate solution has now been found
wherein the decomposition is conducted continuously in
the following stages:

(a) A 2–10 molar excess of barium sulfate is mixed with
sodium carbonate solutions.
(b) The mixture is reacted under a pressure of about
1–10 atmospheres gauge in a heating zone with con-
tinuous withdrawal of the reaction mixture, the re-
action mixture being cooled to temperatures below
100° C. by expansion and direct introduction into
water, preferably at a temperature between about 10
to 35° C., whereby the average residence time of the
reaction mixture in the reaction vessel amounts to
about 5 to about 20 minutes.
(c) The barium carbonate is separated from this solution
by known methods and washed.

Thus the barium sulfate suspension can be rapidly de-
composed with high yields if the reaction mixture is
cooled very quickly to temperatures below 100° C. If
the reaction mixture stands for a relative long time, there
are considerable losses of barium carbonate due to re-
formation of barium sulfate. With continuous decom-
position, the mixture of barium sulfate and soda is
pumped through a reaction vessel which is heated to
temperatures of above 100° C. The reaction solution is
then cooled as quickly as possible and the barium car-

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bonate which has formed is filtered off. Yields of more
than 85% are obtained.

By means of this continuous reaction, it is possible to
reduce considerably the volume of the container or ves-
sel. For example, to decompose 10 tons of barium sul-
fate per day, a reactor space of 0.6 cubic metre is suffi-
cient using 50% barium sulfate sludge as starting mate-
rial, a solution containing 250 g. of sodium carbonate
and a molecular ratio between barium sulfate and sodium
carbonate of 1:2 in the conversion. A residence time of
about 15 minutes in the reactor is required. Carrying
out the same reaction by means of an intermittent proc-
ess, increases the residence time to at least one hour on
account of the necessary starting, cooling and discharge
times. This means that the reactor itself must be in-
creased in size four times, i.e. to 2.5 cubic metres. All
storage and mixing containers must be present in com-
parable sizes. Furthermore, using operation in batches,
it is impossible to recover the heat introduced into the
reaction mixture, whereas this can be effected without any
particular difficulty using continuous operation, for ex-
ample, by using preheaters.

It is preferred to decompose the barium sulfate with a
2–10 molar excess of sodium carbonate and to use pres-
sures of from 1 to 10 atmospheres gauge in the reaction
vessel. The aqueous solutions of sodium carbonate pref-
erably contain 100 to 250 g. per litre of sodium car-
bonate and 5 to 50 g. per litre of sodium hydroxide.
Autoclaves with high speed stirrers can be used as the
reaction vessels. The reaction mixture can be removed
using an adjustable nozzle or a valve which is intermit-
tently opened. Furthermore, the reaction mixture can
also be discharged through a special arrangement of
hydrocyclones.

Example

About 0.4 ton per hour of a barium sulfate waste
sludge is added to a stirrer-type container with a capacity
of 500 litres. The sludge contains 60% of dry substance
of the following composition:

	Percent
BaO	42.0
SO$_3$	23.1
CaO	10.3
MgO	2.17
CO$_2$	8.7
Weight loss on ignition	20.4

73 kg. per hour of 30% hydrochloric acid are run into
the sludge, all impurities such as CaO and MgO being dis-
solved out. This suspension is now run through a rubber
protected rotary filter. The sludge which forms and
which is mainly composed of barium sulfate has the fol-
lowing dry substance composition:

	Percent
BaO	63.2
SO$_3$	33.9
CaO	0.35
MgO	0.12
CO$_2$	0.24

This sludge is now mixed in a vessel with a capacity
of about 500 litres and having an efficient stirrer with
0.635 cubic metre per hour of a solution which contains
220 g. per litre of sodium carbonate and 20 g. per litre
of NaOH. The sodium carbonate-barium sulfate sludge
is passed through a 500-litre storage vessel and then
forced into a stirrer-type autoclave heated to 220° C., a
pressure of 8–10 atmospheres gauge being set up. The
reaction vessel has a capacity of about 200 litres so that
the average residence time is about 12–15 minutes.

The material discharging from the autoclave is sprayed
by means of an intermittently opening valve directly into

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a large quantity of water, being cooled by expansion and quenched to 20–30° C. This large quantity of water is conducted cyclically through a condenser, as much solution being removed as is added by the reacted material sprayed in. The barium carbonate suspended in water and which is formed by the decomposition reaction is filtered off through a rotary filter. The barium carbonate sludge which is obtained has the following composition (as dry substance):

	Percent
BaO	73.9
CO_2	21.1
SO_3	1.5
CaO	0.3
MgO	0.14

The barium carbonate yield using continuous working method is 85 to 90% calculated on the input of barium sulfate. The sludge formed can either be further processed after drying at 100° C. to a powder form containing about 1% of water or can be used as a paste without drying.

I claim:

1. Process for the continuous production of barium carbonate by decomposing barium sulfate under pressure with excess dilute sodium carbonate solution, the steps which comprise mixing the barium sulfate with an aqueous solution of sodium carbonate using a 2 to 10 molar excess referred to the barium sulfate, feeding the mixture continuously into a heating zone, wherein said mixture is boiled under a pressure of 1 to 10 atmospheres with an average residence time of the reaction mixture in the heating zone of about 5 to 20 minutes, withdrawing said mixture continuously from said heating zone under expansion and introducing into water, whereby said reaction mixture is cooled to temperatures below 100° C. and separating off the barium carbonate formed from the aqueous suspension.

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2. Process according to claim 1, wherein the average residence time of the reaction mixture in the heating zone amounts to about 12 to 15 minutes.

3. Process for the continuous production of barium carbonate by decomposing barium sulfate under pressure with excess dilute sodium carbonate solution the steps which comprise mixing the barium sulfate with an aqueous solution containing 100 to 250 g. per litre of sodium carbonate and 5 to 50 g. per litre of sodium hydroxide using a 2 to 10 molar excess of sodium carbonate referred to the barium sulfate, feeding the mixture continuously into a heating zone, wherein said mixture is boiled under a pressure of 1 to 10 atmospheres with an average residence time of the reaction mixture in the heating zone of about 5 to 20 minutes, withdrawing said mixture continuously from said heating zone under expansion and introducing into water, whereby said reaction mixture is cooled to temperatures below 100° C. and separating off the barium carbonate formed from the aqueous suspension.

4. Process according to claim 3, wherein the average residence time of the reaction mixture in the heating zone amounts to about 12 to 15 minutes.

5. Process according to claim 3, wherein the reaction mixture is cooled to temperatures of about 20 to 30° C.

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