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Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
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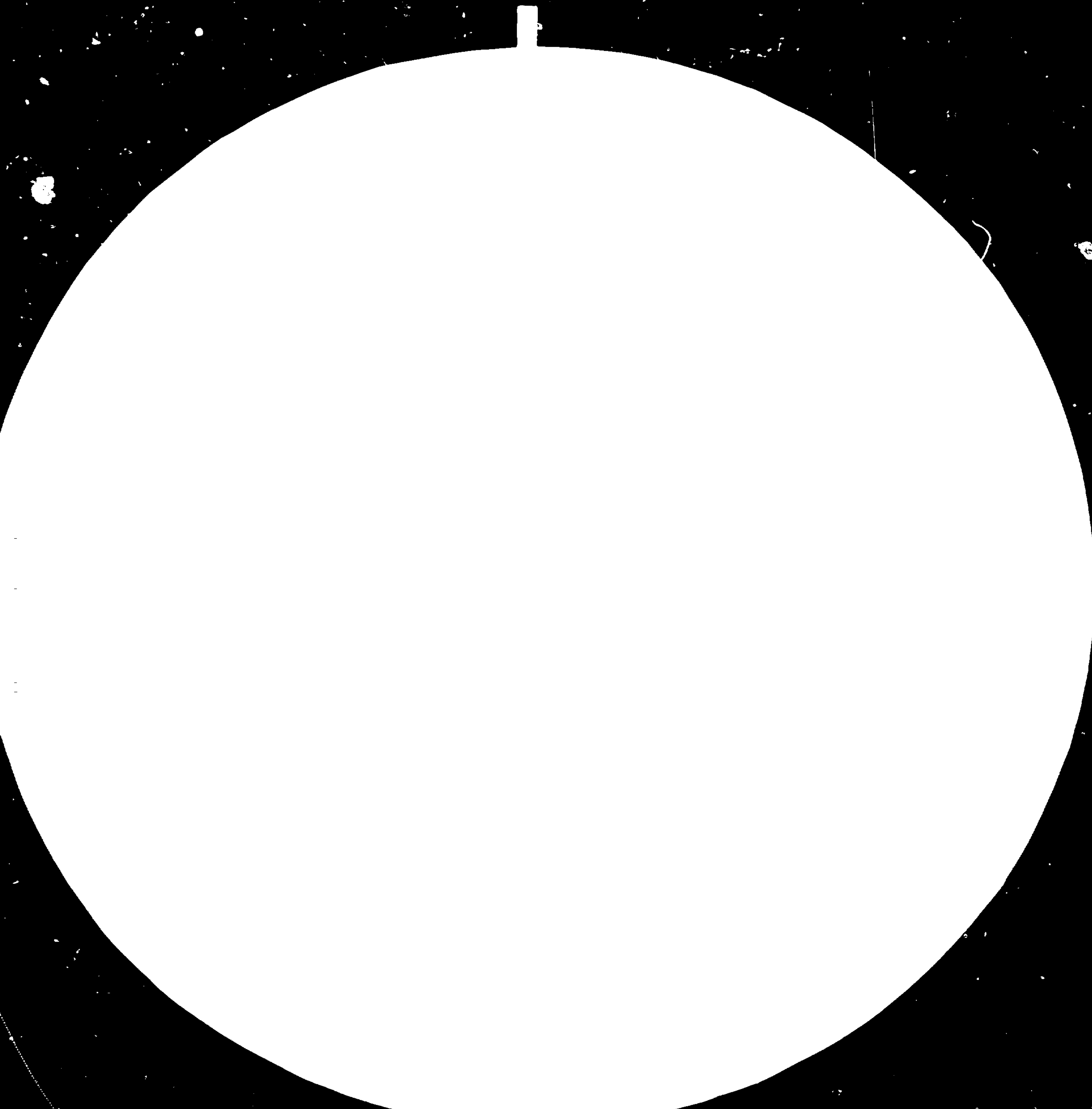

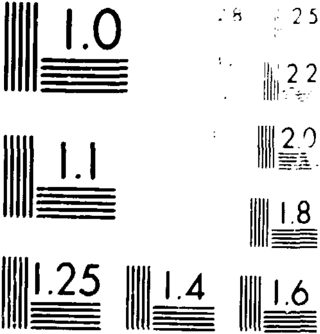
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PERFORMANCE OF VOLATILE SUBSTANCES IN THE KILN*

by

Wieslaw Kurdowski**

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** Professor, Academy of Mining and Metallurgy, Krakow.

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Alkali and Sulphur Cycles in the Kiln

At high temperatures of above 1 100^{o} C in the rotary kiln the alkalis sublimate and pass to the gaseous phase. They react in the gaseous phase with other components, first of all with the chlorine and sulphur dioxide . In cold regions of the kiln they go to be partly condensed on the raw material in the form of sulphates or chlorides and come back to the sintering zone.

In the kiln a dynamic equilibrium settles between the amount of alkalis in the feed and their content in the clinker. It is so-called inner cycle of alkalis, depending on the kiln type as well as on the content of sulphates and chlorides in raw material and in the fuel.

In long, wet process rotary kilns 70 % of alkalis introduced to the kiln remains generally in the clinker, while 30 % leaves the kiln with exit gases /1/. The major part of them precipitates together with the dust in electrostatic collectors. If the dust from electrostatic precipitators is turned back to the kiln, then the so-called external cycle of alkalis comes into being, increasing their content in the clinker. The alkalis in the clinker combine in the first place with the sulphur, forming sulphates. When the molar ration SO_3/R_2O in the feed is lower than 1, the increase in the content of sulphur, introduced to the kiln, for example with the fuel, is accompanied by the growth in alkali content, as the alkali sulphates are only partially decomposed in the sintering zone and have relatively low volatility.

The rise in the content of chlorine, introduced into the kiln, increases the volatility of alkalies and their concentration in the gaseous phase. Alkali chlorides are in the most part undergoing the sublimation in the sintering zone. In these circumstances in long wet and dry process rotary kilns the alkali content of the clinker decreases which makes the recycling of the whole amount of the dust from electrofilters impossible and a part of the dust, usually 25 %, must be removed from the system. The removal of the dust created a serious problem of their individual treating. There are proposed various solutions, from elutriation of the alkalis to the granulation and burning of the dust in a separate kiln; in the latter case the use of the fluid bed to this end seems to be very promising / 2/.

In short, kilns equipped with external suspension preheaters, in result of considerably better mass exchange between gaseous phase and material, the greater part of alkali sulphates is condensed on the grains of the feed and recurred to the kiln / 3/.

In the clinkers from such kilns it remains 90 % of alkalis, and the effect of recycling the dust from the electrostatic precipitators is insignificant, since the alkalis, which have not been condensed in the preheater pass also through the precipitator.In Fig. 1 the cycles of alkalis and chlorine, typical for the four stage cyclone preheater, are shown after Norbom /4/.

The alkali sulphates precipitating in the preheater may form unfavourable build-ups in the inlet chamber, since in the mix K_2SO_4 plus Na_2SO_4 plus $CaSO_4$ the liquid phase appears already at the temperature lower than 800^o C. The formation of build-ups is accompanied with increasing cycle kiln - stage IV cyclone of the dust, lowering considerably the thermal efficiency of the kiln./5/. Highly unfavourably the cholrides act, completely sublimating in the sintering zone and condensing on the grains of the meal in the suspension preheater. The alkali chlorides give only internal cycle: sintering zone - suspension preheater, which leads to a rapid growth of the build-ups in the inlet chamber and to the stoppage of the kiln. For that reason the content of the chlorine in the kiln feed is limited to 0,015 %.

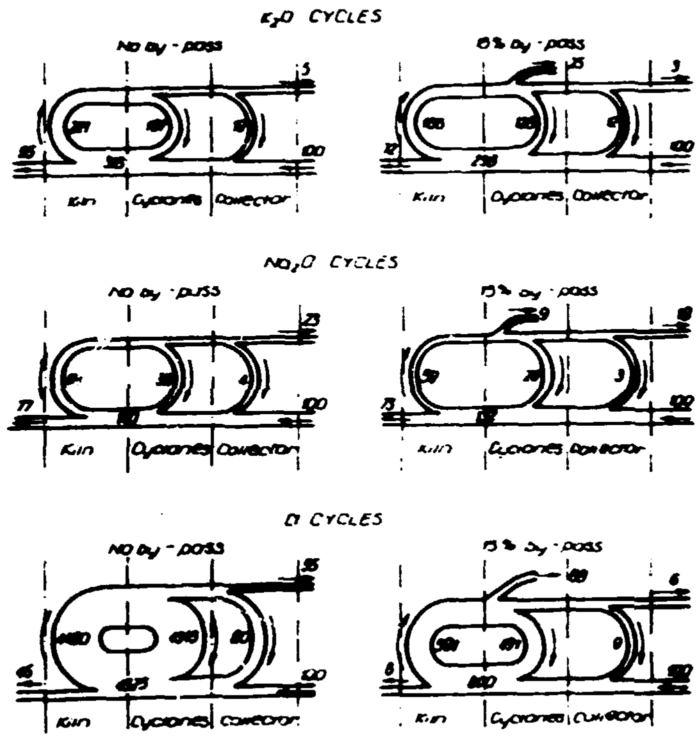

FIG. 1

Cycles of alkalis and chlorine in four stage preneater after Norbom.

The build-ups in the cyclone may be formed also by anhydrite, when the molar ratio $SO_3/R_2O > 1$. These build-ups are soft and easy to remove. Sometimes the obstruction of the preheater may be caused by high alkali content. Great amount of alkalis with low melting point provoke the worsening of the transporting properties of the meal and in such an instance it is advisable to add gypsum or anhydrite to the mix. Of course, the addition of gypsum will increase the alkaii content of the clinker and is inadvisable when by-passing of the gases is employed.

Besides the alkalis and the chlorine also the sulphur makes the cycles in the kiln. The sulphur introduced to the kiln passes in the gaseous phase in the form of SO_2, creating the cycles in the kiln.

As has been stated earlier, the sulphur content of the clinker increases with the amount of alkalis. By deficiency of alkalis the sulphur reacts at temperatures in the range of 600^{o} - $900\ ^{o}C$ with CaO giving $CaSO_4$ which is subjected to secondary decomposition in the sintering zone. This decomposition is not complete, part of $CaSO_4$ passes into the clinker.

In long wet process rotary kilns with the increase of the dusts returned from electrostatic precipitators to the kiln it remains in the clinker about 70 % of the total amount of the sulphur from raw material and fuel. This amount drops to 50 % by removing the dust.

In short kilns with cyclone preheaters it remains in the clinker from 70 to 80 % of the sulphur. This amount - for similar reasons as in the case of alkalis - only slightly depends on the return of the dust from the electrostatic precipitators to the kiln.

The investigations have shown that apart from conventional cycles of alkalis, sulphur and chlorine also some heavy metals make inner cycles in the kiln /6/. It is of far reaching importance in the case of utilization for manufacturing the clinker of waste raw materials or fuels which may evoke the emission of such elements as lead and thallium, noxious for the environment /7/. It holds true particularly in the case of the kilns with Lepol grate preheaters and by higher content of the chlorine /8/. On the other hand, thezinc is incorporated mostly in the clinker, in the amount of 80 - 95 %, and 5-20 % in the dust /6/.

By-passing of the Gases

It is assumed that by the content of chlorine in the raw material exceeding 0,015 % or by major amounts of alkalis the by-passing of gases should be employed. The by-pass should be situated so that the concentration of alkalis, sublimating within the hot part of the kiln, in gases was high, thus before their contact with the raw meal. The exit gases of temperature approximately 1 100^{o} C are introduced in the amount of 5 to 10 % exceptionally up to 20 %, into the by-pass. These gases, containing substantial amounts of the dust, should be immediately cooled to about 450 ^{o} C through mixing with ambient cold air. In this circumstances the alkalis condensate on the grains of the dust and are precipitated in the cyclone. After this operation the gases may be utilized for drying the raw material and led to a joint electrostatic precipitator. For dedusting the gases from the by-pass also a separate electrostatic precipitator is being used.

By-passing of the gases in conventional systems involves considerable increase in the heat - and electric energy consumption. High temperature of the py-passed gases causes that the growth of heat consumption to each per cent of by-passed gases amounts to approximately 20 -24 kJ/kg of clinker. The increase in the electric energy consumption arises from the necessity of employing auxiliary exhauster and cold air fan, and often electrostatic precipitator.

The decrease of alkali content in consequence of by-passing /2/ is depending on the raw material properties which affect the volatility of alkalis, being referred to as volatilization factor. Often for improvement of alkali volatilities the calcium chloride is introduced into the raw material or injected into the kiln /9/.

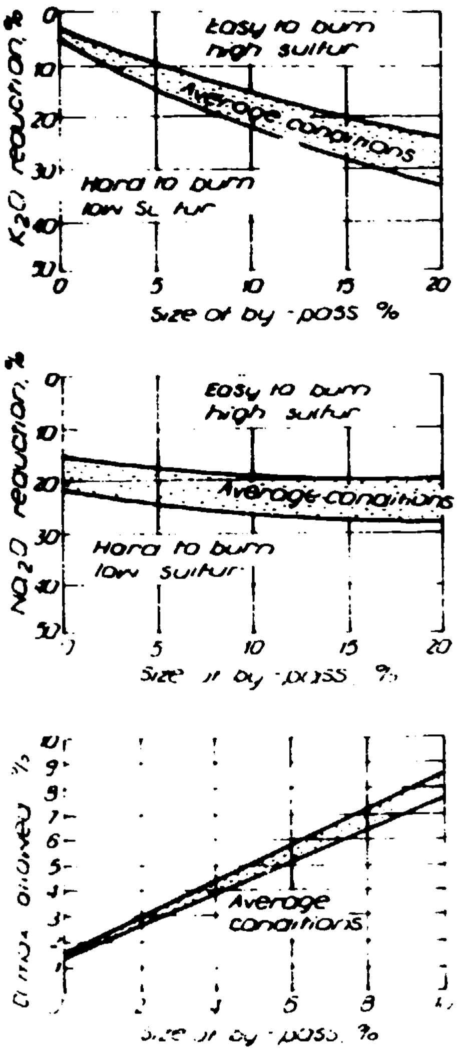

FIG. 2

The decrease of alkali content in function of size of by-pass after Norbom

As mentioned earlier, the precalcining reduces the disturbances in the operation of the kilns, connected with the formation of buildings in the gaseous duct between the kiln and cyclone preheater. However at too high content of harmful components, mainly of the chlorine or when it is necessary to produce a clinker with low alkali content, the by-passing of the gases is employed also in the case of the kilns with precalciners. Highly interesting approach in this field is given by F.L. Smidth Co. /10/. The kiln is equipped only with one line of preheaters /Fig. 3/, co-operating with a precalciner. The whole amount of gases from the kiln is by-passed. It is however relatively small amount of gases, originating only from the firing of 40 % of the fuel and slight, final calcination of the raw mix. For that reason, the concentration of volatile components is very high. By-passing of this small quantity of gases gives considerable decrease of the content of alkali or chlorine in the clinker /Fig. 4/. At the same time the increase in the heat, --

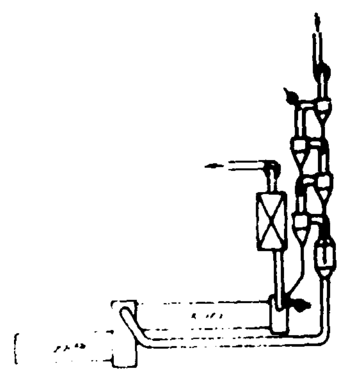

FIG. 3

F.L.S. Kiln with total precalcining and 100 % by-pass of kiln gases.

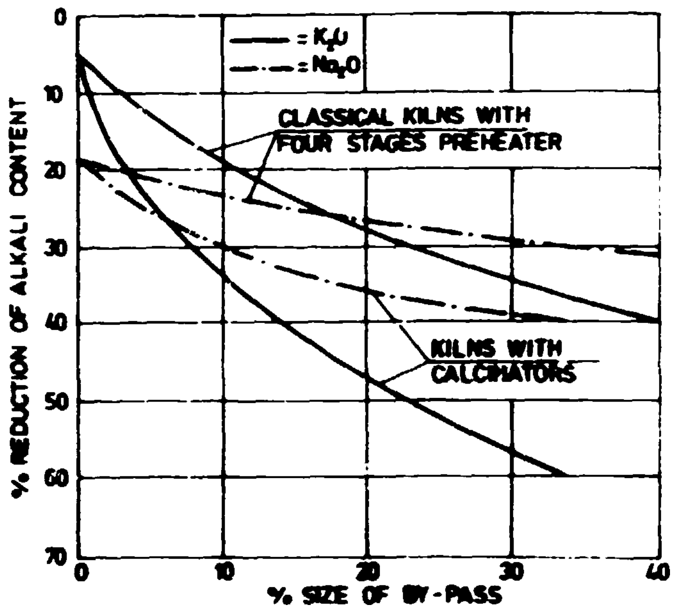

FIG. 4

The decrease of alkali and chlorine content in function of size of by-pass for the kiln with precalcining, after Svendsen.

- consumption is small and amounts to 5.4 - 7.1 kJ/kg of clinker per 1 % of by-passed gases from the kiln, then for 100 % bypass of the gases it attains approximately 630 kJ/kg of clinker /10.11/. The possibility of economical by-passing of gases up to 30 % of the gases gives the kiln with two-stream layout of cyclone preheaters /Fig. 5/. F.L. Smidth Co. delivers also to Egypt one single-stream system, allowing for by-passing 50 - 100 % of kiln gases, with which the overall heat consumption does not exceed 3 770 kJ/kg of clinker /10/.

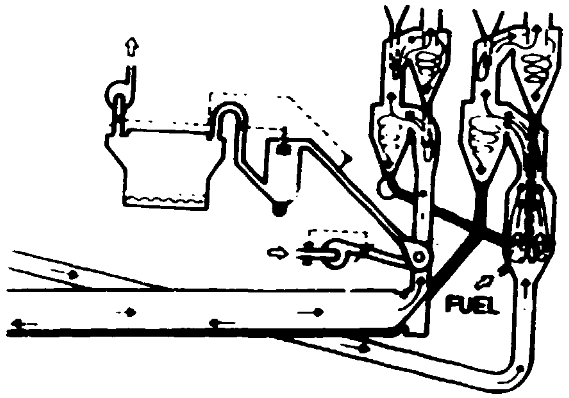

FIG. 5

F.L.S. kiln with two streams preheater and calciner, permitting an economical by-pass up to 30 %.

Humboldt-WEDAG offers also a system with Pyroclon calciner allowing to by-pass 0 - 100 % of kiln gases in an economic way /Fig. 6/(12).

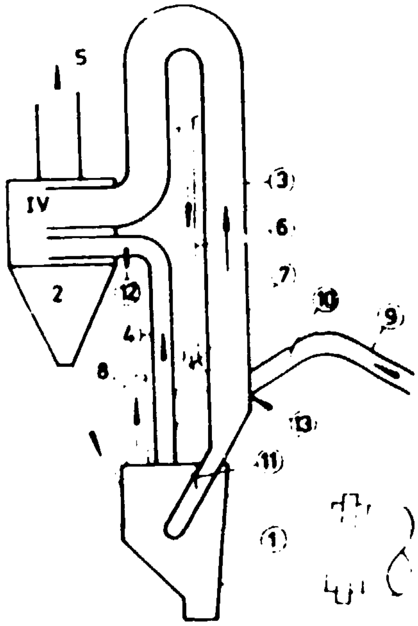

FIG . 6

Pyroclon system for fuels and raw materials rich in sulphur and chlorine.

At a 100 % by-pass the gate 12 is closed and the meal routed exclusively to the reaction system /3/. Kiln gases are discharged over the by-pass /8/. At a 50 % by-pass, half of the kiln gases are directed to the preheater /2/ via the riser pipe /4/. By way of flaps /7/ the raw meal is split onto riser pipe /4/ and calciner /3/ as a function of the gas temperature measured in front of the separator /2/. At a 25 % by-pass, the material chute /11/ is modified to a gas line between kiln and calciner. The kiln waste gases are split onto by-pass /8/, riser pipe /4/ and calciner /3/.

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