

BAKING PARAMETERS AND THE RESULTING ANODE QUALITY

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ABSTRACT

A review of the impact of baking parameters such as heat-up rate, final baking temperature and soaking time on the anode properties relevant to the anode behaviour in the electrolysis pots is presented.

The importance of the flue design and of the baking furnace state, as well as the advantage of efficient baking process control are demonstrated.

INTRODUCTION

Baking represents by far the most expensive stage in the manufacturing of prebaked anodes (1). The goals of the baking process are defined as follows:

- High resistance of the anodes against attack of CO₂ and air, defined by good figures as measured in the reactivity tests (4).
- Low specific electrical resistance.
- Small standard deviations of all physical anode properties.
- Moderate thermal conductivity of the anodes in order to decrease the risk of air burn.
- High productivity and low energy consumption of the baking furnace.

Some of these goals are contradictory a higher final baking temperature normally improves the resistance of the anodes to air attack, but increases the thermal conductivity, resulting in a higher temperature at the top of the anodes in the pots and therefore increasing the risk of airburn.

Considering the fact that the baking parameters are related to the anode raw materials used, an optimization program needs to be repeated every time a major raw material (or anode size) change occurs.

The consequences of poor baking operations on the anode behaviour in the pots can be dramatic. As a result, a large amount of work has been executed in order to understand the phenomenon occurring during the baking process. An excellent summary of the baking process has been published by Hurlen and Naterstad (2). Not yet answered however, is the question of how to choose the different baking parameters: gradient, finishing temperature and soaking time for a given baking furnace and a given brand of green anodes.

Over several years, we have routinely correlated baking parameters with the properties of the anodes produced, during normal production and trials. Taking into account the relationship between anode properties and net carbon consumption (3) guidelines were developed for the determination of optimum baking parameters for given boundary conditions. These findings are reported in this paper.

EXPERIMENTAL

The most important premise for any successful optimization of the baking process is the use of green anodes of constant quality.

The determination of the time/temperature curve for the anodes and of the final anode temperature distribution within the pits have been performed using 16 thermocouples located in the packing materials (5). In tests where this method was not feasible, the relationship between final baking temperature and CO₂ reactivity was determined for the given brand of green anodes on pilot scale samples. This relationship was then used to determine the final anode temperature distribution in the pits.

The anode temperature gradient and the final anode temperature were determined by recording the temperature of a thermocouple located in the packing material at a depth of 1 m below the burner hole level and at the trailing end of the pit, adjacent to the anode and in the middle of the pit. This temperature corresponds approximately to the average temperature measured with the 16 thermocouple procedure described in (5).

The final flue temperature is measured with a pyrometer directed on the flue wall zone located 1.4 m below the burner holes level.

The heat soaking time is defined as the time elapsed between the moment when the flue temperature reaches the final target value and the moment when the burners are stopped.

Finally it has to be mentioned that anodes with good and uniform properties can only be produced with a well designed and well maintained furnace, equipped with an automatic process control system. (7)

In the case of a lack of control of the flue gas temperature, a dramatic peak is observed when the pitch volatiles burn. This induces a maximum anode gradient as high as 20 °C/min as shown in figure 2.

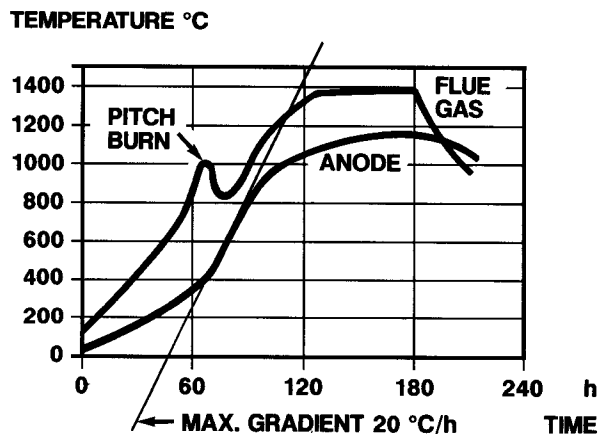


Figure 2. High maximum anode temperature gradient due to uncontrolled pitch volatiles burning.

RESULTS

Anode temperature gradient

Pitch devolatilization occurs in the anode temperature range between 200 and 600 °C. The burning of the pitch fumes has a significant impact on the flue gas temperature and thus also on the anode temperature gradient. A bake furnace process control system is a powerful tool to keep the temperature increase under control. (Figure 1)

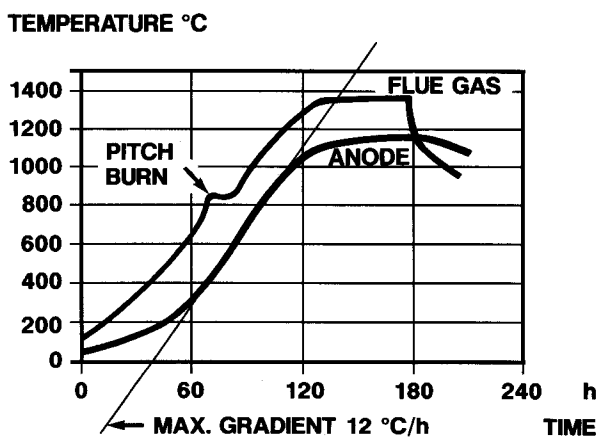


Figure 1. Low maximum anode temperature gradient obtained by appropriate flue gas control.

Due to a release of light binder volatiles during heat up an internal pressure is built up in the anode bulk. With too high a temperature gradient, this effect propagates cracks – sometimes not even detectable by visual inspection – which influence the mechanical properties of the anodes.

As shown in figure 3 the average flexural strength measured on the anode cores decreases sharply above a given temperature gradient. The corresponding standard deviations increase dramatically due to the presence of extended hairline cracks.

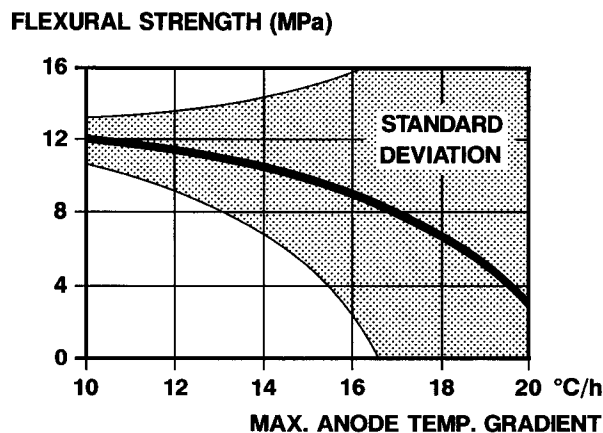


Figure 3. Influence of the temperature gradient on the flexural strength of the anodes.

These cracks can also be detected by the measurement of the specific electrical resistance (SER) of the anodes. In the example shown in figure 4 it can be seen that an increase of the anode temperature gradient from 12 to 16 °C/h causes a 300 % increase of the SER standard deviation.

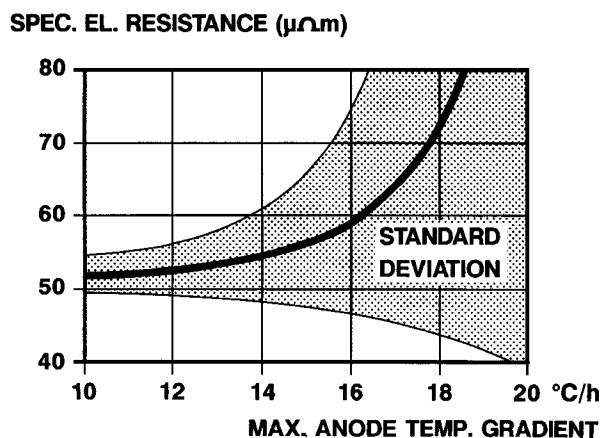


Figure 4. Influence of the temperature gradient on the sp. electrical resistance of the anodes.

The consequences of a too high gradient are unacceptable high baked scrap rate, increase of the energy consumption in the cell and a risk of thermal shocked anodes.

Too low gradients decrease the productivity of the furnace due to the extended firing cycle.

The max. allowed temperature gradient depends on raw materials recipe line and anode dimensions and is in the range of 10 to 14 °C/h.

Scrap rates of baked anodes between 0.3 and 7 % are reported. Such an increase of the scrap rate represents, for a smelter with Al-production of 240,000 tpa, extra costs of 3 million \$/a.

Final anode temperature

Increasing the final anode temperature influences the crystallinity of the binder coke and finally of the coke itself.

As a result of the crystallite size growth the thermal conductivity rises exponentially as a function of the temperature as shown in figure 5.

THERMAL CONDUCTIVITY (W/mK)

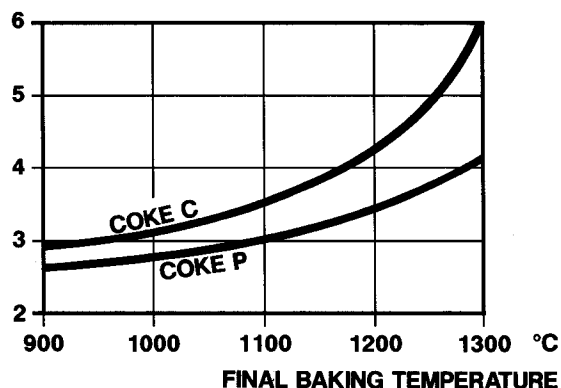


Figure 5. Influence of the anode baking temperature and kind of coke on the thermal conductivity of anodes.

The impact of the final anode baking temperature curves depends on the coke nature (graphitability) while the plateau level at low baking temperature is mainly influenced by the anode porosity i.e. their baked density.

At high temperature level, typically around 1200 °C, desulfurization can be observed especially for high sulfur petroleum coke. As shown in figure 10 a 40 % relative loss in sulfur was determined at 1300 °C for the high sulfur coke 'S' anode while a negligible change was found for the low sulfur coke 'M' anode.

SULFUR CONTENT (%)

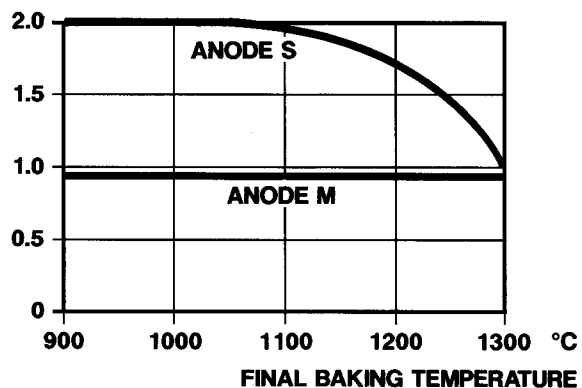


Figure 6. Influence of the final anode baking temperature on the sulfur content of 'S' and 'M' anodes.

The impact of the final anode baking temperature on the CO₂ reactivity is illustrated in figure 7.

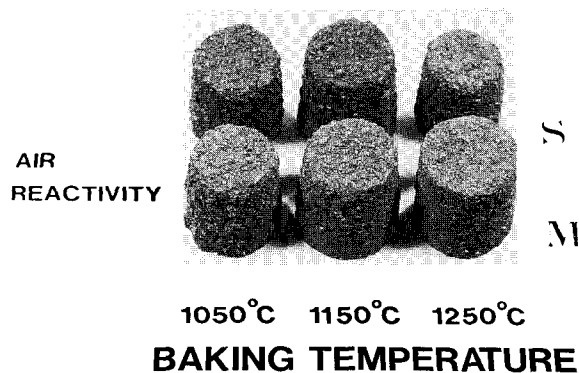
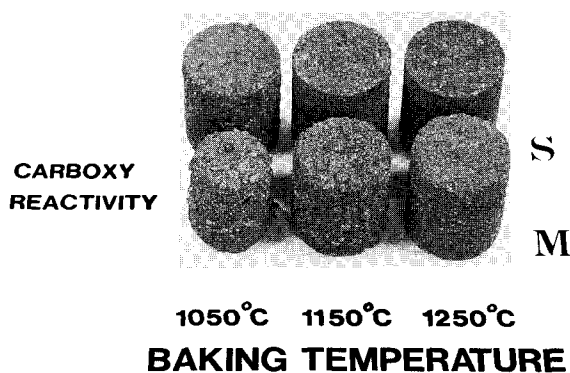
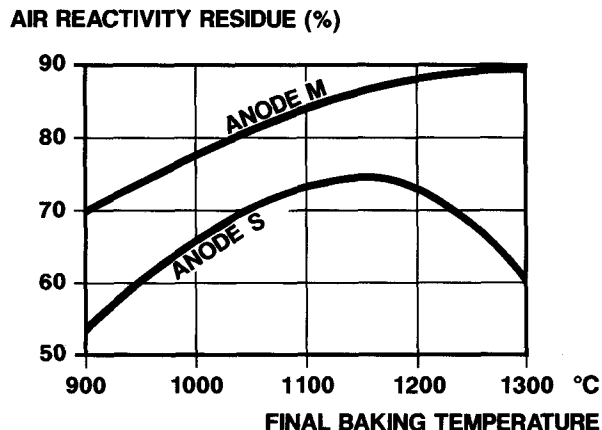
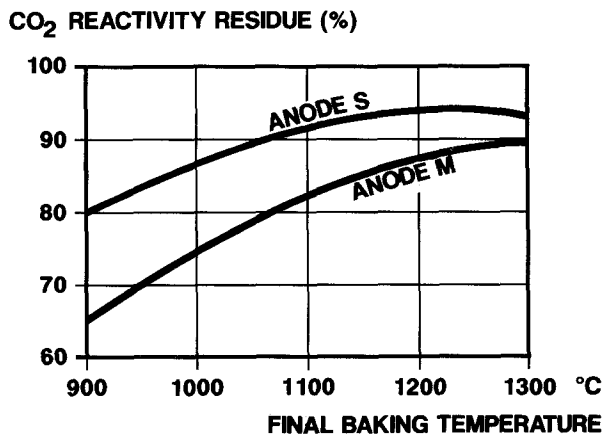


Figure 7. Influence of the final anode baking temperature on the CO₂ reactivity.

Figure 8. Influence of the final anode baking temperature on the air reactivity.

For the CO₂ reactivity the continuous improvement in the residue values is due to the improvement of the selective burning of the binder matrix; the impact of the desulfurization is quite small.

For the air reactivity the increase of porosity due to the sulfur loss above 1150 °C for the high sulfur S anodes adversely affects the air reactivity loss. (Figure 8)

When no desulfurization is observed, as is the case for the M anodes, this deterioration is not observed. Nevertheless an optimum baking temperature can also be defined in this case as any thermal conductivity increase will adversely affect the anode air burn behaviour.

As has been demonstrated for the temperature gradient there is also no absolute value for an ideal final baking temperature which can be defined for all different types of anodes. Depending on the raw materials used, the optimum final baking temperature has to be determined taking into consideration their influence on CO₂ reactivity, air reactivity, (desulfurization), and thermal conductivity. Optimization procedures resulted in final baking temperatures between 1050 – 1200 °C.

Temperature distribution within flues and pits

Degradation of the furnace structure causes severe anode quality deterioration. Leakage or even blocked flues will dramatically deteriorate the temperature distribution within the pits and/or sections and cause huge variations in baked anode quality. (Figure 9)

Properly designed flues in well operated furnaces built with an appropriate brick quality, can easily reach more than 150 fire cycles. (Figure 10).

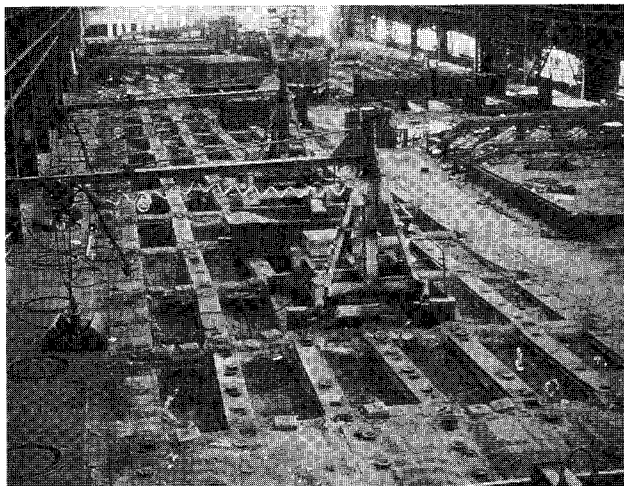


Figure 9. Furnace with severe structure deformation.

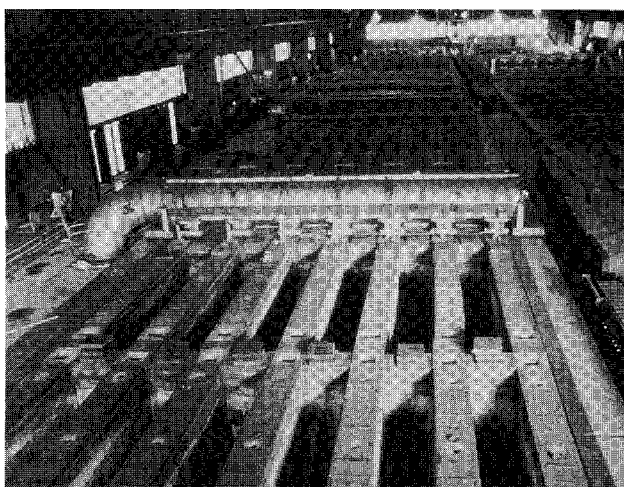


Figure 10. Good aspect of a modern baking furnace after 150 firing cycles.

Uniform heat treatment of the anodes can only be guaranteed for optimized flue design. A proper baffles and bricks arrangement is needed.

The tremendous improvement of the pit temperature distribution due to better flue design is illustrated in figures 11 and 12.

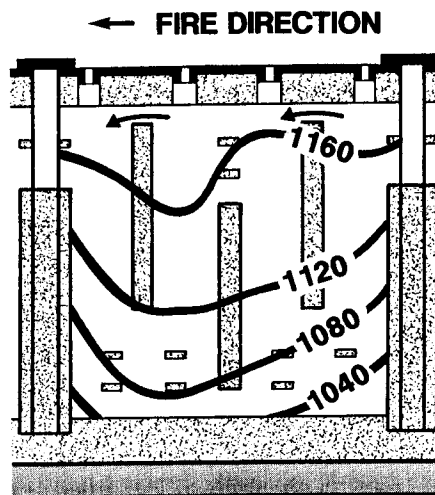


Figure 11. Poor pit temperature distribution due to obsolete flue design.

The large difference between the top and the bottom of the pit is mainly due to the fact that too large a quantity of gas was passing horizontally above the baffles tops.

In an optimized flue design the baffles bricks and pit geometry are arranged to avoid hot spots and cold areas.

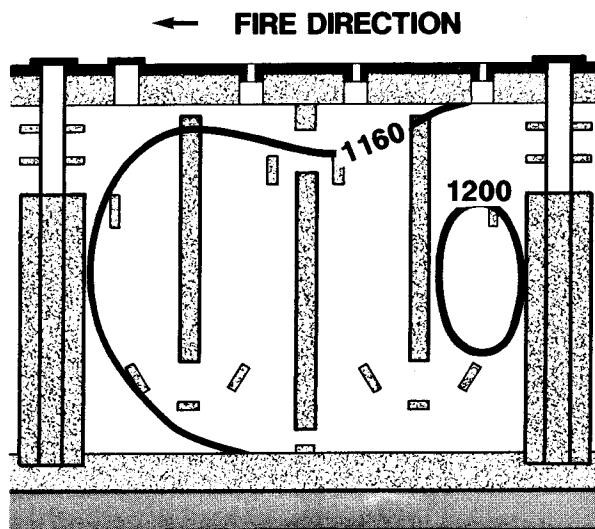


Figure 12. Good pit temperature distribution obtained for an optimized flue design.

Due to the optimized flue design the average anode temperature level is higher and the difference between cold and hot anodes is about three times smaller than with the obsolete design.

Due to the fact that thermal conductivity of refractory, packing material and anodes are rather low and the heat energy to be transferred to the anodes is quite high, the baking operation is a time consuming process.

Longer heat soaking time ensures a better temperature homogenization in the pit. As shown in figure 13, where the target of an average anode temperature was 1175 °C, a difference between coldest and hottest anode temperature less than 80 °C was achieved with a heat soaking time of 50 hours.

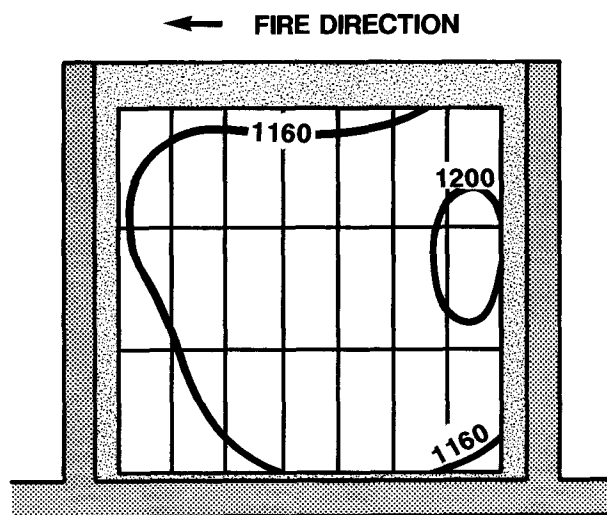


Figure 13. Good temperature distribution of anodes (flue temperature 1260 °C, soaking time 50 H.).

The compensation of a shorter heat soaking time by a higher flue temperature is not recommended. As illustrated in figure 14, a reduction of the heat soaking time from 60 to 20 hours and an increase of the flue temperature of 70 °C leads to a dramatic deterioration of the temperature distribution.

If the average temperature of 1175 °C remains unchanged, the temperature difference between the coldest and hottest anodes rises from 80 to 200 °C.

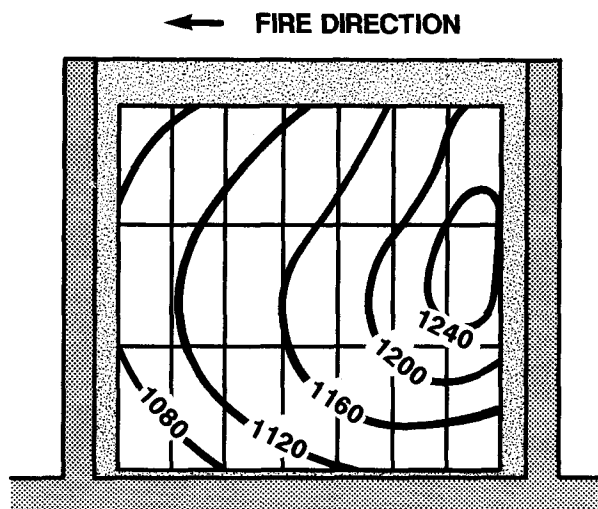


Figure 14. Poor temperature distribution of anodes (flue temperature 1330 °C; soaking time 20 H.).

With this poor temperature distribution, the hottest anode in the pit will show air burn problems in the pots due to the extremely high thermal conductivity, while the coldest anodes will create dusting problems due to underbaking.

Utilizing longer heat soaking times than are needed for an appropriate temperature distribution in the pit has the disadvantage that the firing cycle has to be extended, reducing the output of the furnace.

Financial impact of a bake furnace optimization

Final anode baking temperatures below 50°C below the optimum have a negative impact on anode net consumption between 15 and 20 kg C/t Al.

50 °C too high a final anode baking temperature increases the energy input about 10% and at the same time reduces the flue life by 30%.

Taking into account that the total cost of a deterioration in the anode quality is approximately three times the cost of the extra anode consumption, sub optimum operation of the bake furnace in a plant with a metal output of 240,000 tpa leads to extra costs of US \$ 8 million/a. Obviously testing anodes in order to determine the optimum baking furnace parameters is money well spent.

CONCLUSIONS

It has been shown that baking parameters have a tremendous influence on the quality of the baked anodes.

Too high anode temperature gradients increase the standard deviations of el. resistance and flexural strength dramatically (cracks). The allowed max. anode temperature gradient between 200 and 600°C should not exceed 10 to 14°C/h.

A too low final baking temperature or too short heat soaking time leads to selective air and CO₂ burning of the anodes in the pots. This problem can be detected by a deterioration in the levels and standard deviations of the reactivity values. A too high final baking temperature creates airburn problems and can be detected by measuring the degree of desulfurization and the thermal conductivity. Appropriate levels are in the range of 1050 – 1200 °C

An optimal temperature distribution in the flues and the anodes can be obtained by appropriate flue design, refractory maintenance, correct heat soaking time and last but not least, by a powerful computerized process control system. The difference between the hottest and coldest anode temperature should not exceed 100°C.

The optimum parameters for a given baking furnace and a given kind of green anodes can be determined by applying well established testing methods. Such an optimization should be executed every time the anode raw materials are changed.

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