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DIRECT CAUSTICIZATION OF KRAFT BLACK LIQUOR SOLIDS WITH TiO_2 IN A FLUIDIZED BED

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ABSTRACT

Direct causticization of kraft black liquor with TiO_2 in the solid-state was studied. The experiments using kraft black liquor solids (KBLS) were conducted in a pilot fluidized bed operating at 700 - 900°C under gasification conditions. A calculation procedure was established to determine the $4Na_2O{\cdot}5TiO_2$ and $Na_2O{\cdot}3TiO_2$ contents of the bed residual solids (BRS). The experimental work focused on the effects of temperature, air ratio, Na_2O/TiO_2 molar ratio and bed TiO_2 particle size on the direct causticization reactions. The results showed that for gasification conditions the pentatitanate yield did not change substantially at temperatures above 750°C, but was significantly lower at lower temperatures. An air ratio of about 0.3 was found to give the highest direct causticization of KBLS. The caustic yield increases with increasing Na_2O/TiO_2 molar ratio, while the TiO_2 particle size did not significantly influence the pentatitanate yield for size fractions smaller than 150 µm. The results indicate that the formation of $4Na_2O{\cdot}5TiO_2$ during direct causticization of KBLS still follows the diffusionally controlled shrinking-core model, after an initial relatively rapid formation of $Na_2O{\cdot}3TiO_2$.

Key words: direct causticization, kraft black liquor recovery, titanium dioxide, pentatitanate, trititanate

INTRODUCTION

Conventional kraft recovery is an integral part of the kraft process by which the pulping chemicals and energy in waste kraft black liquor (KBL) are recovered. Although it has served the industry well, the method has several major drawbacks in terms of economy (too high capital cost), safety (smelt-water explosion hazard) and environmental impact (emission of reduced sulfur gases) [1]. The search for alternative processes has been widely pursued over the last twenty years. These new recovery methods include alternatives which replace the conventional recovery boiler, and alternatives which replace the conventional (wet) lime causticizing process. By far the most promising alternative for conventional kraft black liquor combustion is the gasification of kraft black liquor [2,3], while a possible alternative for the conventional lime causticization is the direct causticization technology [4,5].

The direct causticization technology used for sulfur-free pulping, called the Direct Alkali Recovery System (DARS), uses Fe_2O_3 as the direct causticizing agent [6]. Since Fe_2O_3 reacts with sulfur and is reduced by carbon in KBL char, the DARS process cannot be used for kraft recovery. Thermodynamic analysis has shown that TiO_2 is likely the only chemical which can be applied for direct causticization of KBL [5]. A number of small-scale experimental studies have been conducted on the reaction kinetics of Na_2CO_3 with TiO_2 [7-9] and on KBL combustion in the presence of TiO_2 [10]. The latter investigation has shown that NaOH can be produced by direct causticization of KBL with TiO_2.

Practically, it is of interest to combine direct causticization of KBL by TiO_2 or sodium titanates with gasification of KBL. Firstly, a high temperature needed for both gasification and direct causticization can be realized in a single reactor. Secondly, and most importantly, direct causticization with TiO_2 produces high melting point products which minimize the smelt formation problem associated with high temperature gasification processes. Thirdly, formation of sodium titanates would reduce sodium emission, a serious problem in conventional kraft recovery.

Pilot testing of KBL gasification with direct causticization by TiO_2 in a fluidized bed has been reported earlier [11]. The present follow-up study emphasizes the influences of operation variables on KBL direct causticization, such as air ratio, temperature, Na_2O/TiO_2 molar ratio and TiO_2 particle size, for a better understanding of this combined recovery process.

CHARACTERIZATION OF DIRECT CAUSTICIZATION

Direct Causticization Reactions

Depending on the feed molar ratio, the reaction between Na_2CO_3 and TiO_2 leads to various sodium titanates. The direct causticizing reaction of Na_2CO_3 by TiO_2 can be represented generally as:

$$a\ Na_2CO_3 + b\ TiO_2 = aNa_2O{\cdot}bTiO_2 + a\ CO_2\uparrow \qquad (1)$$

According to the phase diagrams of Na_2O-TiO_2 system [12,13], a limited number of $aNa_2O{\cdot}bTiO_2$ are stable at temperatures between 700 and 1000°C: $Na_2O{\cdot}TiO_2$ (sodium metatitanate), $4Na_2O{\cdot}5TiO_2$ (sodium pentatitanate), $Na_2O{\cdot}3TiO_2$ (sodium trititanate), and $Na_2O{\cdot}6TiO_2$ (sodium hexatitanate). Bamberger and Begun [14] have confirmed these findings by synthesizing sodium titanates and analyzing them thoroughly. Therefore, the direct causticizing reactions of Na_2CO_3 with TiO_2 may be represented by the following series of consecutive reactions:

$$Na_2CO_3 + 6\ TiO_2 = Na_2O{\cdot}6TiO_2 + CO_2\uparrow \qquad (2)$$

$$Na_2CO_3 + Na_2O{\cdot}6TiO_2 = 2\ (Na_2O{\cdot}3TiO_2) + CO_2\uparrow \qquad (3)$$

$$7\ Na_2CO_3 + 5\ (Na_2O{\cdot}3TiO_2) = 3\ (4Na_2O{\cdot}5TiO_2) + 7\ CO_2\uparrow \qquad (4)$$

$$Na_2CO_3 + 4Na_2O{\cdot}5TiO_2 = 5\ (Na_2O{\cdot}TiO_2) + CO_2 \uparrow \quad (5)$$

Among the titanates, the formation of $Na_2O{\cdot}6TiO_2$ requires the lowest stoichiometric Na_2O/TiO_2 molar ratio. Since the present fluidized bed experiments are operated in a semi-batch mode with all TiO_2 charged at the start, followed by steady addition of sodium as part of kraft black liquor solids (KBLS), the overall Na_2O/TiO_2 molar ratio in the fluidized bed reactor will be low initially so that formation of $Na_2O{\cdot}6TiO_2$ is expected. However, because the reaction of Na_2CO_3 with TiO_2 is limited by diffusion of Na_2CO_3 into the particle and follows a shrinking-core model [9,15], the actual Na_2O/TiO_2 molar ratio at the surface of the particles should be much higher than the overall Na_2O/TiO_2 molar ratio in the reactor. Furthermore, the high reactivity of $Na_2O{\cdot}6TiO_2$ with Na_2CO_3 will lead to rapid formation of $Na_2O{\cdot}3TiO_2$ [9]. It is our understanding that the reaction front of reaction (2), moving inwards to the center of the particle, is closely followed by the reaction front of reaction (3). Therefore, it is expected that only small quantities of $Na_2O{\cdot}6TiO_2$ is present in the reacting particles, and only at the beginning of the experiments. The previous experiments [15] showed that $Na_2O{\cdot}6TiO_2$ was detected, but it rapidly disappeared when more Na_2CO_3 was fed to the reactor. Since quantification of $Na_2O{\cdot}6TiO_2$ is difficult and since its existence is insignificant for the present work, the reactions (2) and (3) involving $Na_2O{\cdot}6TiO_2$ will be combined as:

$$Na_2CO_3 + 3\ TiO_2 = Na_2O{\cdot}3TiO_2 + CO_2 \uparrow \quad (6)$$

There is also ample evidence in the literature [7,14,17,18] showing that the formation of $Na_2O{\cdot}TiO_2$ is very slow and a relatively long reaction time (several hours) is needed even at a temperature as high as 935°C, and that $Na_2O{\cdot}TiO_2$ is possibly converted to $4Na_2O{\cdot}5TiO_2$ at temperatures below 1000°C in the presence of CO_2 at certain partial pressures which are typical for KBL gasification gas. Therefore, the formation of $Na_2O{\cdot}TiO_2$ by reaction (5) is unlikely to be significant during KBLS gasification in the present fluidized bed at temperatures between 700 and 900°C. The reaction mechanism has thus been simplified, and only the reactions (6) and (4) will be considered in this study. In other words, the titanate products which will be of interest in this study are $Na_2O{\cdot}3TiO_2$ and $4Na_2O{\cdot}5TiO_2$.

NaOH can be generated when the sodium titanate products contact with water. The overall hydrolysis reaction of $4Na_2O{\cdot}5TiO_2$ is:

$$3\ (4Na_2O{\cdot}5TiO_2) + 7\ H_2O = 14\ NaOH + 5\ (Na_2O{\cdot}3TiO_2) \quad (7)$$

$Na_2O{\cdot}3TiO_2$ is insoluble in water and can be reused for direct causticization as shown by reaction (4) [7,9,15].

Since the bulk of sodium in KBLS is rapidly converted into Na_2CO_3 during pyrolysis and subsequent gasification of kraft black liquor solids [19], it may be expected that there are many similarities between direct causticization during KBL gasification and that of pure Na_2CO_3. Important differences are that the liquid-like behaviour of KBLS during pyrolysis will lead to much better penetration of the sodium into the TiO_2 particles, and that the presence of other elements in KBLS, such as sulfur and potassium, will lead to a more complex chemistry.

In a realistic gasification process using direct causticization, TiO_2-based materials will be used as a sorbent for the capture and recovery of sodium. Although the starting material is virgin TiO_2, the bulk of the sorbent will consist of $Na_2O{\cdot}3TiO_2$ that is recycled in the recovery system. The process will be basically a repetition of reaction (4) taking place in the gasification reactor, and reaction (7) taking place in a separate leaching unit. Only a small amount of TiO_2 will be added as a make-up stream.

Direct Causticization Parameters

Four parameters, caustic yield, titanate yield, pentatitanate yield and causticizing efficiency, are defined to characterize the direct causticization process. The caustic yield (Y_c) is the amount of caustic generated per amount of sodium fed to the reactor:

$$Y_c = \frac{\text{mol NaOH generated}}{\text{mol Na input}} \tag{8}$$

It can be shown that starting from virgin TiO_2 the maximum caustic yield is 0.583, if the direct causticization and hydrolysis reactions described by equations (6), (4) and (7) go to completion. On the other hand, if $Na_2O{\cdot}3TiO_2$ rather than TiO_2 is used as causticizing agent as in an industrial application, then only the direct causticization and hydrolysis reactions (4) and (7) apply, and the maximum caustic yield will be 1.0.

The titanate yield (Y_t) is defined as:

$$Y_t = \frac{\text{titanates generated}}{\text{effective sodium}} = \frac{N_4T_5 + NT_3}{N_4T_5 + NT_3 + Na_2CO_3} \tag{9}$$

whereby NT_3 and N_4T_5 represent $Na_2O{\cdot}3TiO_2$ and $4Na_2O{\cdot}5TiO_2$, respectively. NT_3, N_4T_5 and Na_2CO_3 are all in moles of Na_2O. Y_t can vary between 0 and 1, and characterizes how much of the total sodium available for direct causticization is converted into sodium titanates.

The pentatitanate yield (Y_{N4T5}) is defined as:

$$Y_{N4T5} = \frac{\text{pentatitanate generated}}{\text{effective sodium}} = \frac{N_4T_5}{N_4T_5 + NT_3 + Na_2CO_3} \tag{10}$$

again with NT_3, N_4T_5 and Na_2CO_3 expressed in moles of Na_2O. This parameter describes the amount of sodium in the form of the desired product $4Na_2O{\cdot}5TiO_2$ as a fraction of the total sodium available for direct causticization.

The last parameter is the conventional causticizing efficiency (E_c) defined as:

$$E_c = \frac{\text{NaOH generated (all as } Na_2O)}{\text{NaOH generated} + Na_2CO_3 \text{ remaining}} \times 100 \tag{11}$$

This quantity is used when comparing the present results with those of conventional lime-based causticization.

Procedure for Determination of the Composition of Bed Residual Solids

A calculation procedure is developed to determine the composition of the bed residual solids (BRS) based on the chemical analyses of the BRS and the leachate formed by hydrolysis of the BRS. Based on the arguments given previously, it will be assumed that the BRS consists of the following four "compounds": $4Na_2O{\cdot}5TiO_2$, $Na_2O{\cdot}3TiO_2$, TiO_2 and Na_2X, whereby Na_2X represents all sodium salts such as Na_2CO_3, Na_2S, $Na_2S_2O_3$, Na_2SO_4, Na_2Cl_2, etc., i.e. all those other than the titanates. Chemical analysis of BRS [15] provides four measurable quantities: (1) $N_{Na/BRS}$, the number of moles of sodium per gram of BRS; (2) $N_{Ti/BRS}$, the number of moles of titanium per gram of BRS; (3) $N_{Na/L}$, the number of moles of sodium in the leachate per gram of BRS; and (4) $N_{OH/L}$, the number of moles of hydroxide ions in the leachate per gram of BRS.

The four compounds, $4Na_2O{\cdot}5TiO_2$, $Na_2O{\cdot}3TiO_2$, TiO_2 and Na_2X can all be expressed in terms of these four measurable quantities, $N_{Na/BRS}$, $N_{Ti/BRS}$, $N_{Na/L}$ and $N_{OH/L}$ [16]:

$$N_{NX} = \frac{1}{2}(N_{Na/L} - N_{OH/L}) \tag{12}$$

$$N_{NT45} = \frac{12}{14} N_{OH/L} \tag{13}$$

$$N_{NT3} = \frac{1}{2} N_{Na/BRS} - N_{N4T5} - N_{NX} = \frac{1}{2}(N_{Na/BRS} - N_{Na/L} - \frac{10}{14} N_{OH/L}) \tag{14}$$

$$N_{TiO2} = N_{Ti/BRS} - \frac{5}{4} N_{N4T5} = 3N_{NT3} = N_{Ti/BRS} - \frac{3}{2}(N_{Na/BRS} - N_{Na/L}) \tag{15}$$

Where N_{NX} is the number of moles of Na_2X per gram of BRS, N_{N4T5} is the number of moles of Na_2O in $4Na_2O{\cdot}5TiO_2$ per gram of BRS, N_{NT3} is the number of moles of Na_2O in $Na_2O{\cdot}3TiO_2$ per gram of BRS, and N_{TiO2} is the number of moles of unconverted TiO_2 per gram of BRS.

EXPERIMENTAL

The experiments of direct causticization of KBL were performed at 700 - 900°C in a pilot fluidized-bed facility. The fluidized-bed gasifier has an internal diameter (ID) of 0.1 m and length of 0.58 m in the reaction zone, and 0.2 m ID in the freeboard zone with a length of 0.64 m. The system was operated in a semi-batch mode. TiO_2 particles were preloaded in the fluidized-bed reactor at a total weight of 1.2 - 1.4 kg. Kraft black liquor solids, with a feed rate from 0.5 to 0.75 kg/hr in the different experiments, were injected continuously into the fluidized bed. The total fluidizing gas flow was controlled at 13 to 19 L/min (STP) for the individual runs. In the gasification experiments, the bed was fluidized with a mixture of air and nitrogen to control the air ratio between 0 and 0.55. These experiments are identified as AG##. Pyrolysis experiments in which the fluidizing gas was pure nitrogen are labelled as PY##. The feed rate of KBLS as well as the reactor temperature was maintained as constant as possible during the experiments. The composition of the product gases was determined gas chromatographically and by infrared analysis during the course of experiments.

At the end of each experiment the bed residual solids were analyzed for anions S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$ and CO_3^{2-} by ion chromatography and potentiometric titration. The titanate composition

and unconverted TiO_2 of the BRS were determined by the calculation procedure described previously. In some cases, bed samples were taken during the runs. Details about the analytical procedures as well as the operation of the pilot plant are given elsewhere [11,15,16]. The overall carbon and sodium mass balance closures for most of runs are less than 5%, verifying the accuracy of the experimental procedures and analytical methods [16].

The titanium dioxide used for this study was R-Granular rutile with a purity of 98% obtained from Tioxide Inc. The overall particle size ranged from 77 to 250 µm. In the individual runs, a narrow particle size range was used such as 77 - 85, 105 - 125, 125 - 149, 149 - 177 and 177 - 250 µm. The KBLS produced by pulse drying of oxidized hardwood weak kraft black liquor from Nackawic Pulp Co. consisted of spherical particles with diameters ranging from 10 to 40 µm. The analysis of KBLS is shown in **Table 1**.

Elemental composition, wt%		Inorganic species and other, wt%	
C	32.3	CO_3^{-2} as C	1.39
H	3.76	S_2^{-2} as S	0.0
O	35.8	SO_3^{-2} as S	0.233
Na	18.2	SO_4^{-2} as S	1.03
S	2.97	$S_2O_3^{-2}$ as S	1.43
Cl	0.655	Organic C [a]	30.9
K	3.04	Organic S [b]	0.277
Total	96.7	Moisture	4.28

[a] By difference of total carbon and carbonate;
[b] By difference of total sulfur and inorganic sulfur.

Table 1. Analysis of dry kraft black liquor solids.

Due to the existence of a small amount of potassium in KBLS, there is an inherent error in the previous calculation procedure that hydroxide ions may be contributed from hydrolysis of potassium titanates which will be generated by direct causticization of potassium. The magnitude of this error in $N_{OH/L}$ was experimentally estimated as less than 3% [16]. Since it is a small error, relative to the error in most sodium measurements, potassium chemistry is not taken into consideration separately.

RESULTS AND DISCUSSION

Effect of Air Ratio

The effect of air ratio on titanate yield is summarized in **Table 2**. It lists a number of experiments which differ mainly in the air ratio used. Run AG8 is also included in the table despite a rather larger particle size, since the effect of particle size on titanate yield is not significant over the present size range as will be shown later. Two almost identical pyrolysis runs (PY2 and PY3) except for temperature are also listed in the table because their median temperature (852°C) is very close to that of the other four runs (854°C). Thus, the median values of the parameters for

these two pyrolysis runs, which are listed in the table under run no. PY_{med}, are used as an indication for a pyrolysis run at about 850°C.

Run No.	T (°C)	Na_2O/TiO_2 (mol/mol)	Rxn.time (min)	TiO_2 size (µm)	**Air ratio**	Y_{N4T5}	Y_{NT3}[a]	**Organic carbon (%wt)**
PY2	833	0.20	83	125-149	**0**	**0.30**	**0.68**	**2.08**
PY3	871	0.20	73	125-149	**0**	**0.59**	**0.40**	**1.50**
PY_{med}[b]	852	0.20	~78	125-149	**0**	**0.45**	**0.54**	**1.79**
AG12	849	0.26	106	125-149	**0.31**	**0.67**	**0.32**	**0.025**
AG2	853	0.27	98	105-125	**0.33**	**0.68**	**0.31**	**0.024**
AG8	857	0.27	121	177-250	**0.41**	**0.58**	**0.41**	**0.0**
AG4	857	0.26	140	105-125	**0.51**	**0.49**	**0.50**	**0.009**

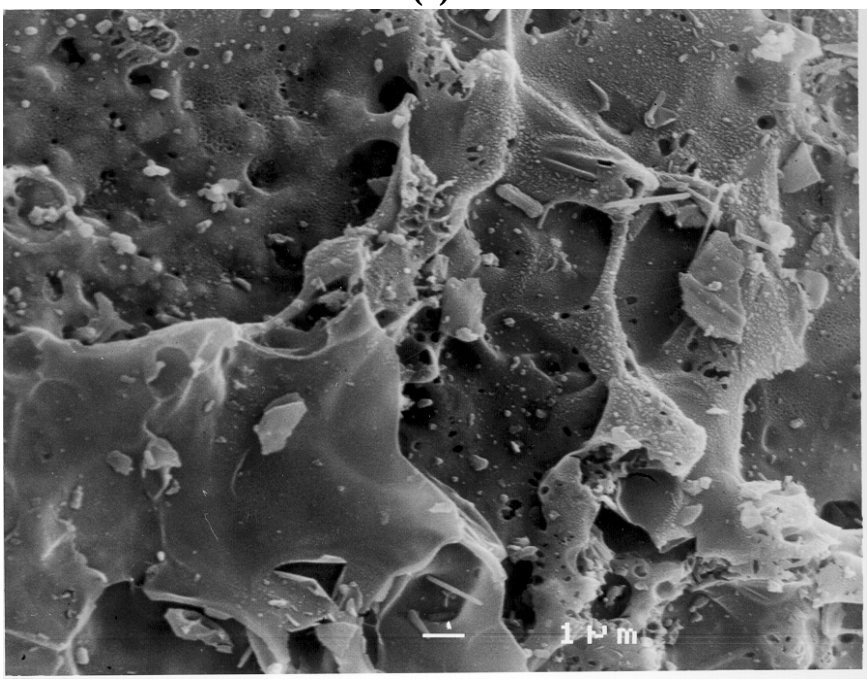
[a] $Y_{NT3} = Y_t - Y_{N4T5}$

[b] PY_{med} is the median of PY2 and PY3.

Table 2. Comparison of air ratio effect on titanate yield.

It can be seen from Table 2 that pentatitanate yield (Y_{N4T5}) reaches a maximum at an air ratio of 0.31 - 0.33. The reason for the lower Y_{N4T5} at an air ratio of zero is possibly due to the fact that a layer of char deposits on the particle surface as a result of incomplete carbon gasification at a low air ratio. This layer acts as an additional diffusion resistance for Na_2CO_3, and thus the direct causticization rate and caustic yield were significantly reduced. As shown in Table 2, the carbon content of the BRS of the runs PY2 and PY3 runs is much higher than that of the other runs. Furthermore, the SEM picture in **Figure 1(a)** for the pyrolysis experiment at 833°C shows that the particle surface is almost completely covered with a layer of ungasified char, while in **Figure 1(b)** for the pyrolysis experiment at 871°C, the surface is exposed due to the decrease of carbon deposit at a higher pyrolysis temperature.

(a)



(b)



Figure 1. SEM micrographs showing carbon char coated on the BRS surface. (a) Pyrolysis at 833ºC for 73 minutes.

The likely explanation for the decreased value of Y_{N4T5} at the higher air ratio of 0.51 is that the formation of pentatitanate from trititanate by reaction (4) may be inhibited by the higher CO_2 concentration in the fluidizing gas atmosphere at the higher air ratio. For example, the measured CO_2 concentrations of the gasification gas for AG12, AG2, AG8 and AG4 runs are 7.5, 8.9, 10.3 and 11.9%, respectively, generally increasing with decreasing Y_{N4T5}. The effect that an increased CO_2 partial pressure decreases the caustic yield (hydroxide yield) was earlier noticed by Kiiskila

[8]. He reported that at 900°C the hydroxide yield decreased almost by a factor two when the CO_2 partial pressure increased from zero to 0.2 bar.

The above results pertaining to the operating air ratio are important for practical kraft black liquor recovery with direct causticization. Since $4Na_2O{\cdot}5TiO_2$ is the desired product, it suggests that the gasification air ratio should be controlled between about 0.3 and 0.45 to optimize pentatitanate yield. These conditions coincide with the generation of a product gas with a highest heating value [16].

Effect of Temperature

The effect of temperature on the pentatitanate yield (Y_{N4T5}) is shown in **Figure 2**. Each symbol in the figure represents a set of data points from different runs but with a similar air ratio and Na_2O/TiO_2 molar ratio. It can be seen that for the experiment done at the lowest temperature of 706°C (solid squares), with a Na_2O/TiO_2 molar ratio of 0.23 and an air ratio of 0.47 (AG1), Y_{N4T5} is only 0.23, indicating that the kinetics of formation of $4Na_2O{\cdot}5TiO_2$ is slow at this relatively low temperature. When the temperature is increased to 834°C under a similar Na_2O/TiO_2 molar ratio and air ratio, the value of Y_{N4T5} increases to 0.59. This increase is mostly due to the effect of temperature, since the small difference in air ratio between these two experiments can be expected to result in only a small change in Y_{N4T5}.

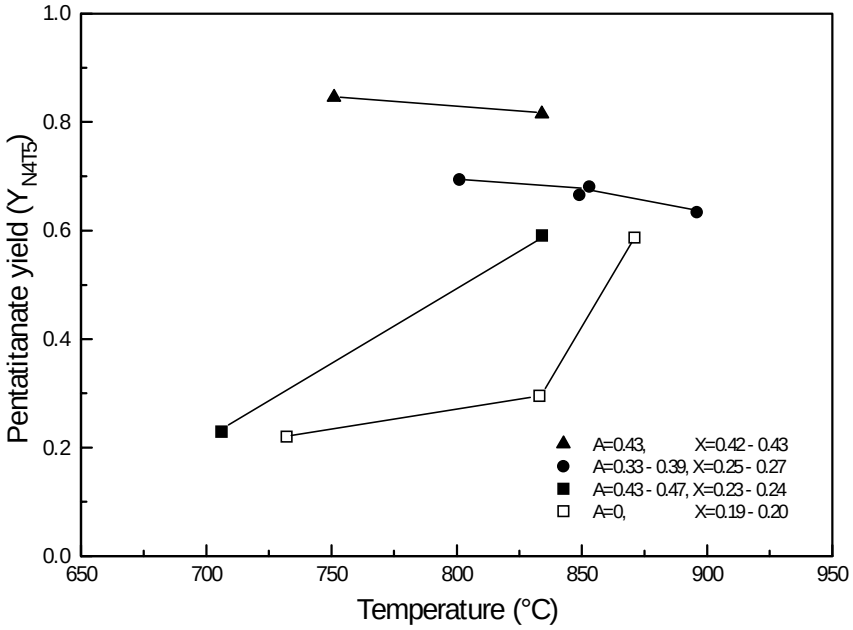
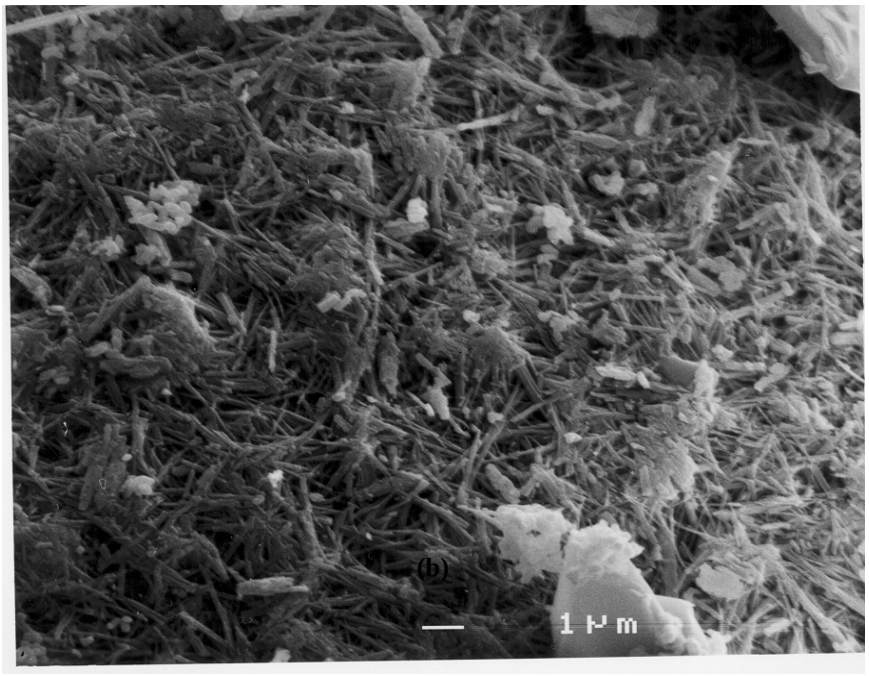


Figure 2. Effect of temperature on pentatitanate yield. A = air ratio, X = Na_2O/tiO_2.

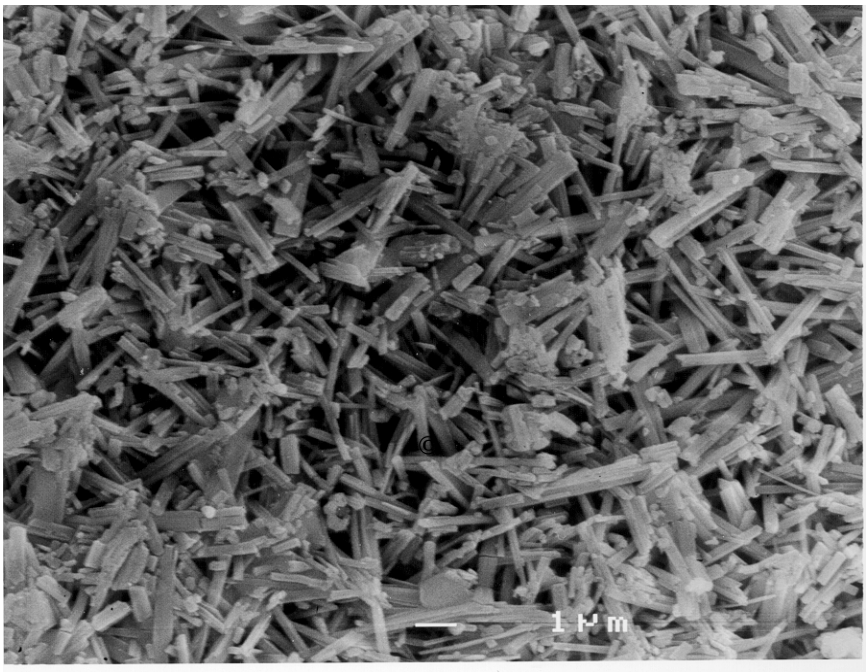
When the Na_2O/TiO_2 ratio is slightly higher at 0.25 - 0.27 (solid circles) or significantly higher at 0.42 - 0.43 (solid triangles), the results of Y_{N4T5} show that with a further increase in temperature above 750°C Y_{N4T5} does not increase anymore, but decreases slightly. Although the displayed decreases are of the same order of magnitude as the estimated experimental error (5-10%), the observed decreasing trend with increasing temperatures for both curves implies something other than the experimental error. One possible reason for Y_{N4T5} decrease is the enhanced agglomeration and sintering of the bed particles with the temperature increase. The effect of temperature on the surface morphology of the bed particles can be illustrated by the SEM

pictures of the BRS samples presented in **Figure 3(a-d)**. These samples were obtained from the different gasification runs mainly with different temperatures. It can be seen that at 700°C the surface is covered with thin needle-like structures. With increasing temperature, similar needle or rod-like structures are found with a larger length and diameter than the needles found at 700°C, depending on the reaction temperature. It is clear that the higher the temperature, the more fused structures can be seen. The explanation is that at a lower temperature, crystals grow preferentially in one direction, while at higher temperatures crystals grow in the other directions as well to form rods. In any case, crystal growth causes pore closure and increases the resistance of Na_2CO_3 transport.

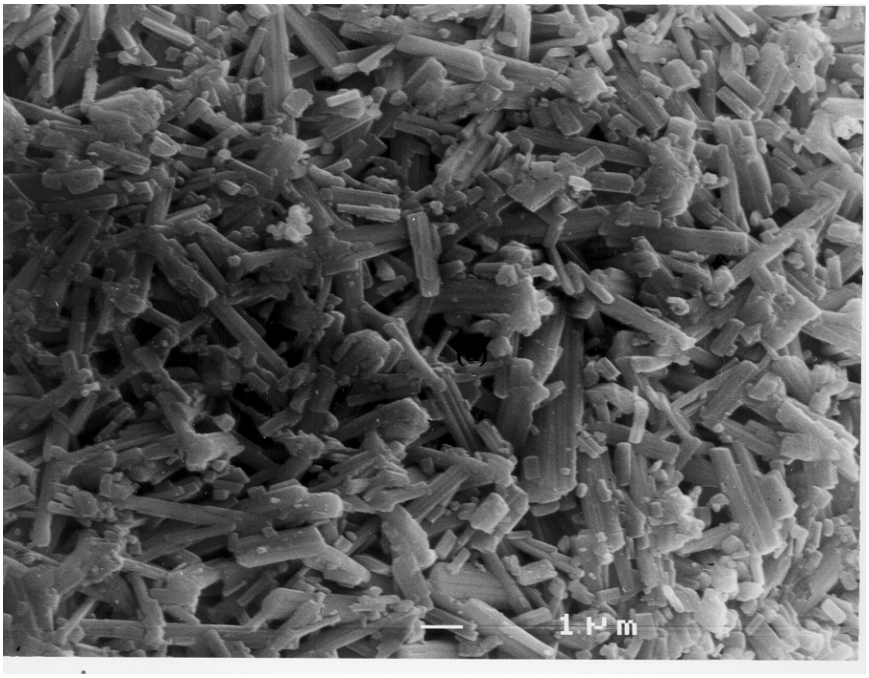
(a)



(b)



(c)



(d)

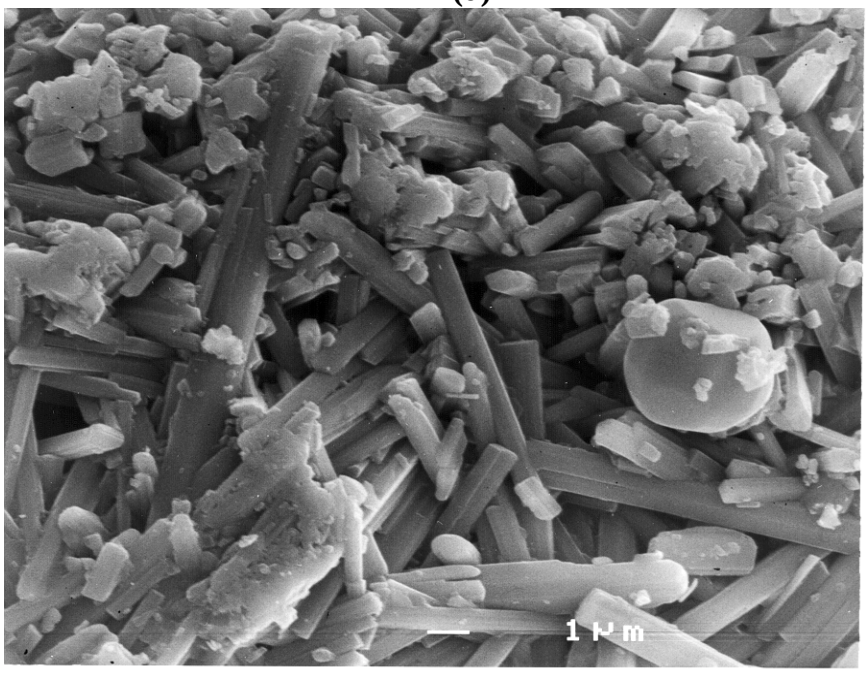


Figure 3. SEM micrographs showing surface morphology change of BRS as a function of temperature.
a) at 700°C for 110 minutes and Na_2O/TiO_2 = 0.23.
b) at 800°C for 110 minutes and Na_2O/TiO_2 = 0.26.
c) at 850°C for 100 minutes and Na_2O/TiO_2 = 0.27.
d) at 900°C for 110 minutes and Na_2O/TiO_2 = 0.25.

At pyrolysis conditions (open squares in Figure 2), the influence of temperature on Y_{N4T5} is significantly different. At a temperature of 833°C, a Y_{N4T5} of 0.30 is obtained which is much lower than that of any gasification experiment done at a similar temperature. The likely explanation for the reduced direct causticization at this temperature is the presence of ungasified char on the outer surface of the TiO_2 particles, which inhibits fast penetration of Na_2CO_3 as discussed before. At the highest temperature of 871°C pyrolysis yields a significantly higher value of Y_{N4T5} of 0.59, evidently due to the reduced accumulation of the ungasified organic carbon on the surface at this higher temperature as demonstrated in Figure 1(b).

It is also worth noting that for gasification runs, in the entire range of temperatures between 700 and 900°C, the titanate yields (Y_t) are 0.99 or higher. Pyrolysis runs show lower titanate yields, but only slightly: between 0.95 at 730°C and 0.98 at 871°C. This result means that very little Na_2CO_3 remained and the direct causticization reaction (6) for formation of $Na_2O{\cdot}3TiO_2$ is fast under gasification conditions, even though the formation of $4Na_2O{\cdot}5TiO_2$ is relatively slow at 700°C.

Effect of Na_2O/TiO_2 Molar Ratio

The Na_2O/TiO_2 molar ratio is determined based on the overall contents of sodium and titanium fed during the experiment. The influence of the Na_2O/TiO_2 molar feed ratio on caustic yield is shown in **Figure 4**. Runs at the lowest temperature and the lowest and highest air ratios were excluded in order to minimize the effect of temperature and air ratio. The caustic yield (Y_c) is used here instead of Y_{N4T5} for direct evaluation of caustic generation per sodium input. It is obvious that a higher Na_2O/TiO_2 molar ratio leads to a higher caustic yield despite sizable differences in air ratio, temperature and TiO_2 particle size. The results in Figure 2 show that Y_{N4T5} increases to values above 0.8 when the Na_2O/TiO_2 molar ratio increases from 0.25 - 0.27 to 0.42 - 0.43. It should be noted that a Na_2O/TiO_2 molar ratio of 0.8 is required for stoichiometric formation of $4Na_2O{\cdot}5TiO_2$. Stoichiometric $4Na_2O{\cdot}5TiO_2$ corresponds to a theoretical maximum caustic yield of 0.583. The data in Figure 4 indicate that at low Na_2O/TiO_2 molar ratios of about 0.1 most of the sodium is in the form of sodium trititanate, but at Na_2O/TiO_2 molar ratios of about 0.35 or higher most of the sodium is in the form of pentatitanate. The important implication of Figure 4 is that formation of $4Na_2O{\cdot}5TiO_2$ already occurs at a low Na_2O/TiO_2 molar ratio, before conversion of all TiO_2 to $Na_2O{\cdot}3TiO_2$ is completed. The dot line in Figure 4 gives the calculated caustic yield when the direct causticization reactions proceed from TiO_2 to $Na_2O{\cdot}3TiO_2$ and then to $4Na_2O{\cdot}5TiO_2$ sequentially and uniformly throughout the particle. It can be seen that all the experimental data points are well above this theoretical line. This indicates that the direct causticization reactions do not take place uniformly throughout the particle, but from outside to inside, according to a multiple shrinking-core model. This behavior of KBLS direct causticization is exactly the same as found in the direct causticization of pure Na_2CO_3 in the same fluidized-bed reactor reported by Pels et al. [15].

Because the reaction mechanism follows a shrinking-core model, the Na_2O/TiO_2 molar ratio should be higher at the surface of the particles than overall. This was confirmed by SEM-EDS (Scanning Electron Microscopy with Energy Dispersive Analyses of X-Rays). Results of selected samples are summarized in **Table 3**. The depth of the analyses on the surface is about 1 µm. The very high Na_2O/TiO_2 molar ratio of 2.03 for sample AG5-S3 in Table 3 implies that besides $4Na_2O{\cdot}5TiO_2$ a significant amount of unreacted Na_2CO_3 must be present at the particle surface, or that unstable sodium titanates with a high Na_2O/TiO_2 ratio may be formed.

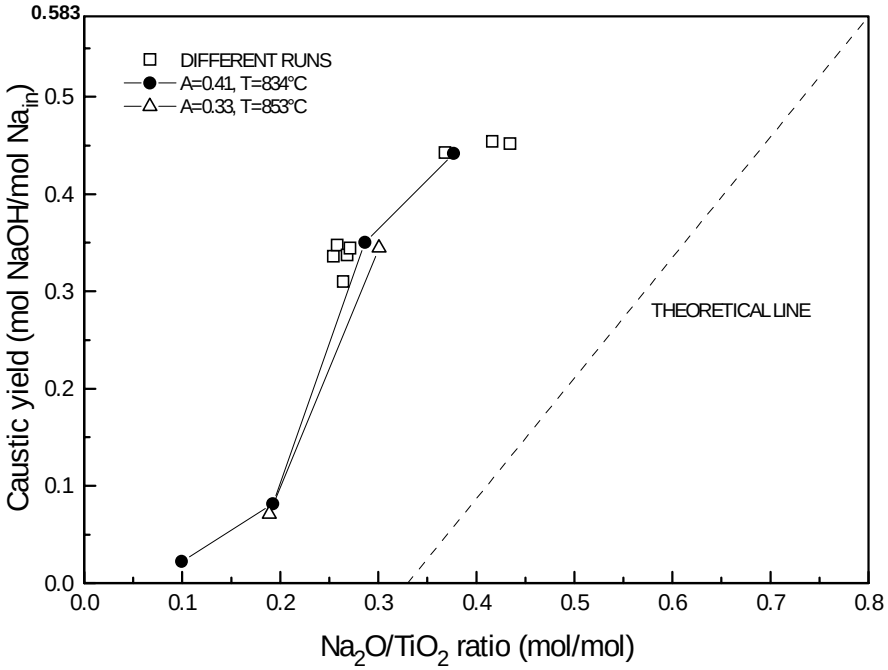


Figure 4. Effect of Na_2O/TiO_2 molar ratio on caustic yield. For unspecified runs, air ratio (a) = 0.31 - 0.43, T = 751 = 896°C. The dotted line indicates the theoretical caustic yield based on a sequential reaction mechanism.

Sample No.	Overall Na_2O/TiO_2 (mol/mol)	Surface Na_2O/TiO_2 (mol/mol)
AG2-S1	0.17	0.62
AG2-S2	0.27	0.80
AG5-S3	0.43	2.03

Table 3. Comparison of overall and surface Na_2O/TiO_2 molar ratio.

Effect of TiO_2 Particle Size

The influence of TiO_2 particle size on pentatitanate yield is shown in **Table 4**. Normally the particle size is a critical parameter for diffusion limited solid-state reactions. However, in this study increasing TiO_2 particle size leads to a decrease in Y_{N4T5} only for the largest particle size fraction (177-250 µm). This suggests that in the present study the size of the TiO_2 particles is not the important parameter. This apparent contradiction can be understood when it is realized that the different size TiO_2 particles consist of agglomerates of micro particles of a diameter of about 0.3 µm [15]. Probably, the major diffusion limitation is located in these micro particles and that the liquid-like behavior of KBLS leads to rapid impregnation throughout the agglomerates as long as they are small.

Run No.	T (°C)	Rxn. time (min)	Air ratio	Na_2O/TiO_2 (mol/mol)	**TiO_2 size (μm)**	**Y_{N4T5}**	**Y_{NT3}**
AG11	851	112	0.31	0.27	**75 - 88**	**0.65**	**0.34**
AG2	853	98	0.33	0.27	**105- 125**	**0.68**	**0.31**
AG12	849	106	0.31	0.26	**125 - 149**	**0.67**	**0.32**
AG8	857	121	0.41	0.27	**177 - 250**	**0.58**	**0.41**

Table 4. Effect of TiO_2 particle size on pentatitanate yield.

Causticizing Efficiency

The causticizing efficiency of the conventional lime-based causticization is practically about 80 - 86% [20]. The causticizing efficiencies for white liquor obtained from leaching of samples produced in this study, shown in **Figure 5**, are substantially higher. Efficiencies of about 98% are obtained under gasification conditions, almost independent of the gasification temperature. Even at 700°C where low Y_c and Y_{N4T5} were measured, an efficiency of 94% is still obtained.

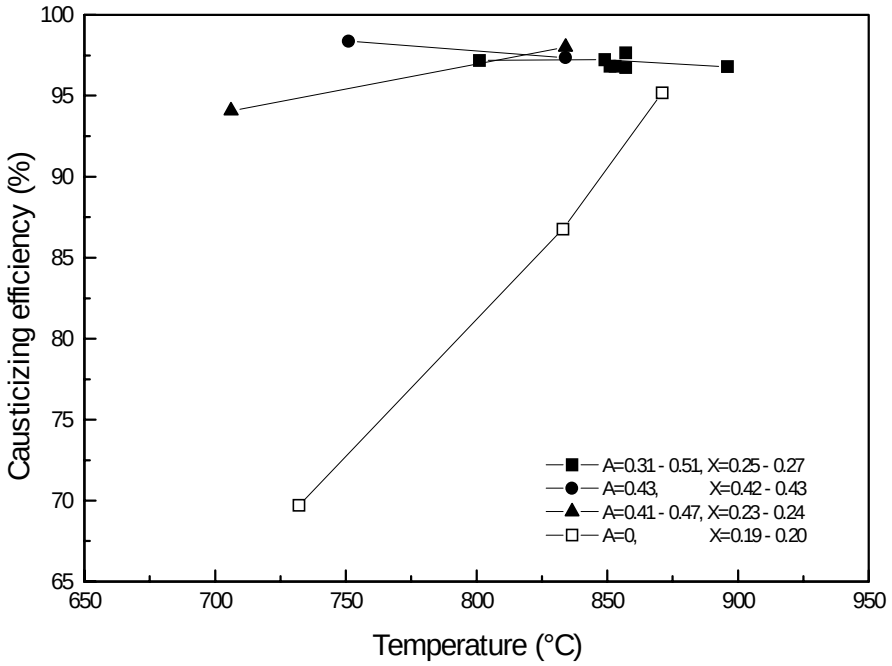


Figure 5. Effect of temperature on causticizing efficiency. Air = air ratio, X = Na_2O/TiO_2 molar ratio.

Under pyrolysis conditions, the causticizing efficiency appears to be more temperature dependent. As discussed before, the likely reason for this is the diffusion resistance created by the char layer on the surface of the TiO_2 particles at these conditions. A higher pyrolysis temperature reduces the organic carbon yield and thus the diffusion resistance, thereby leading to an increased causticizing efficiency, similar to those found under gasification conditions.

It should be noted that the results in Figure 5 are somewhat misleading because it only considers whether Na_2CO_3 is converted into titanates, but does not account for the conversion of $Na_2O{\cdot}3TiO_2$ into $4Na_2O{\cdot}5TiO_2$. Since only $4Na_2O{\cdot}5TiO_2$ leads to the generation of caustic, the high causticizing efficiency at 700°C can still lead to a low pentatitanate yield as shown in Figure 2 and lower caustic yield overall. At 750°C or higher, an air ratio of 0.3 to 0.45 and a Na_2O/TiO_2 feed ratio larger than about 0.35, the desired $4Na_2O{\cdot}5TiO_2$ is the dominant titanate product. In those cases, both caustic yield and causticization efficiency are high.

SUMMARY AND CONCLUSIONS

Direct causticization of kraft black liquor solids (KBLS) with TiO_2 during gasification has been realized in a pilot scale fluidized bed at temperatures between 700 and 900°C. A calculation procedure was established to quantify the amounts of $4Na_2O{\cdot}5TiO_2$ and $Na_2O{\cdot}3TiO_2$ in the bed residual solids (BRS) based on measurements of the total sodium content in the BRS and the sodium and hydroxide concentrations in the aqueous leachate of BRS.

The experiments under gasification conditions show that at a relatively low temperature of about 700°C the formation rate of $4Na_2O{\cdot}5TiO_2$ is very low. An increase in the temperature to about 750°C leads to a substantial increase in pentatitanate yield. A further increase in temperature does not significantly affect pentatitanate yield.

At an air ratio of about 0.3, the pentatitanate yield reaches a maximum. A lower air ratio results in incomplete carbon gasification, so that a layer of char forms an additional diffusion resistance for the Na_2CO_3 to reach the reaction front. On the other hand, at a higher air ratio the formation of pentatitanate from trititanate is likely inhibited by the higher CO_2 partial pressure. Therefore, for practical kraft black liquor recovery with direct causticization, the gasification air ratio should be controlled between about 0.3 and 0.45 so as to gasify all the carbon but also to minimize the CO_2 formation.

A higher Na_2O/TiO_2 molar ratio in BRS samples corresponds with a higher caustic yield. Even at a relatively low Na_2O/TiO_2 molar ratio of about 0.35, the pentatitanate yield is significant. It was deduced that a fast formation of $Na_2O{\cdot}3TiO_2$ takes place, followed by a relatively slow conversion of $Na_2O{\cdot}3TiO_2$ to $4Na_2O{\cdot}5TiO_2$. The reaction mechanism proceeds according to a multiple shell shrinking-core model with unreacted TiO_2 at the center of the core. The much higher Na_2O/TiO_2 molar ratio at the surface of the BRS particles as measured by EDS analysis is in agreement with this hypothesis.

TiO_2 particle size does not have a significant influence on the pentatitanate yield as long as it is smaller than 150 µm. This is most likely because the different size TiO_2 particles all consist of agglomerates of micro particles of about 0.3 µm in diameter. The main transport resistance is most likely in these micro particles. Since the $4Na_2O{\cdot}5TiO_2$ yield decreases for the largest particle size of 177 - 250 µm, a particle size smaller than 150 µm is recommended for direct causticization of KBL in a fluidized bed.

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