

Reactivation of Partially Sulphated CFBC Ash and Limestone with Steam and Liquid Water

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Abstract

It is not unusual for ashes produced from fluidized bed combustion technology to contain 20-30% of unreacted CaO following limestone addition to remove SO₂ *in situ*. In order to improve the sorbent utilization, reactivating the unused CaO with liquid water or steam is a promising technique. This study presents the results of reactivating partially sulphated CFBC ash (both bed ash and fly ash) with liquid water and steam. The hydrated samples were subsequently re-sulphated in a TGA with simulated flue gas to evaluate the results of reactivation. The current results show that, while liquid water and steam successfully hydrate and reactivate the unreacted CaO in the bed ash, ashes so treated sulphated to widely different extents. Attempts to reactivate fly ash with hydration have failed, although it is extremely reactive. In addition, experiments were also carried out on various limestones, which were sulphated in the lab to their maximum conversion degree, followed by hydration and re-sulphation. This study shows that reactivation is possible for all of these types of limestones.

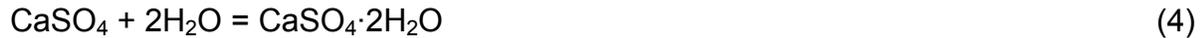
Introduction

Circulating fluidized bed combustion (CFBC) is an effective technology for burning high-sulphur fuels with SO₂ removal *in situ* by limestone addition. SO₂ is captured *via* the following two-step process [1]:



The limestone particles calcine from a low-porosity solid to a porous CaO matrix, and then sulphate. When the sulphate layer forms, the pores are filled and blocked by the CaSO₄ product, preventing SO₂ reaction with the unreacted CaO core. Ca utilization of CFB technology is typically from 20% to 40% and the ash usually contains significant CaO content, from 20% to 30%, in addition to CaSO₄.

During hydration, reactions for the CaO/CaSO₄ system are dominated by direct hydration of the CaO component (3), whereas the formation of gypsum (4) is slow and can normally be ignored in hydration experiments lasting for hours.



This paper attempts to provide a comprehensive evaluation of the effect of hydration with liquid water and steam on reactivation of the ashes from an industrial CFBC boiler and synthetic samples obtained from long-term sulphated limestones.

Experimental

Materials

The partially sulphated material, including bed ash (BA) and fly ash (FA), was from the 165 MWe CFBC boiler firing petcoke and coal blends at Point Aconi, Nova Scotia, Canada. Table 1 gives the chemical analysis of BA and FA. The as-received bed ash was sieved and the particle size fraction of 150-300 μm was used in the majority of reactivation experiments presented in this paper, as this size accounted for about 62% of the entire mass. Particle size of 300-600 μm , accounting for 23% of the sample, was subjected to scanning electron microscope (SEM) analysis after hydration. The FA had a mean size of about 40 microns.

Table 1. Chemical analysis on CFBC ash (wt.%)

	FA	BA (150-300 μm)
SiO ₂	15.9	6.8
Al ₂ O ₃	4.7	2.2
CaO	46.4	52.6
SO ₃	19.2	32.6
Loss on fusion	9.1	3.1
Sum	99.998	100.00
CaO utilization	30	43
Carbon analysis		
Total carbon	4.3	0.1
Carbonate carbon	0.73	0.09

The sorbent used in this boiler for capturing SO₂ was a local calcitic limestone, Kelly Rock (KR), and its CaCO₃ content is typically about 90% (Table 2). Other limestones, *i.e.*, Cadomin (C), Havelock (H) and Graymont (G), were also used in this study. The limestone was crushed and screened to a size of 250-425 μm . Results of the chemical analysis of the limestones are given in Table 2.

The initial sulphation of limestone was carried out in a tube furnace at 850°C overnight (about 16 h) using 5 g of fresh limestone with simulated sulphating gas (SO₂ 1%, O₂ 3%, N₂ balance). Before sulphation, the limestone samples were heated at 850°C for 2 h in N₂ environment to obtain full calcination. Sulphation times were chosen to be relatively long to ensure that the fresh limestones had reached a “maximum” conversion degree,

signifying that although the samples were in fact only partially sulphated, the reaction rate at the time was slow enough to consider the reaction as being completed.

Table 2. Chemical analysis of fresh and sulphated limestones[†] (wt.%)

	KR	KRS	C	CS	H	HS	G	GS
SiO ₂	3.45	3.21	0.94	1.02	1.0	1.05	1.64	2.06
Al ₂ O ₃	1.11	1.09	0.36	0.42	0.13	0.38	0.49	0.58
CaO	51.3	49.9	53.9	57.1	51.3	54.4	53	58.6
MgO	0.48	0.49	0.23	0.26	3.14	3.34	0.61	0.69
SO ₃	<0.1	39.3	<0.1	32.4	<0.1	36.2	0.22	32.1
Loss on fusion	41.8	4.77	43.2	8.49	43.7	4.28	42.6	5.1
Sum	98.7	99.4	98.9	100	99.7	100	99.0	99.8
CaO utilization	-	55.2	-	39.7	-	38	-	38.4

[†]XS means overnight-sulphated samples

Determination of free lime and Ca(OH)₂

Free lime is defined as the sum of CaO + Ca(OH)₂ in the sample, which is expressed as CaO percent [2]. It was determined chemically (the sucrose method) in this study, as described in ASTM C-25, lime index. The sample was first slaked and dispersed in boiling water. During treatment with a solution of sucrose, free lime was converted to soluble calcium sucrate, which was then determined by titrating the filtrate with 0.1 M hydrochloric acid and phenolphthalein as the indicator.

Ca(OH)₂ was determined by a Cahn 1000 thermogravimetric analyzer (TGA). Nitrogen was used as carrier gas at a flowrate of 100 mL/min. Ca(OH)₂ decomposes in the TGA over the temperature range of 370-420°C.

Hydration with liquid water

Liquid water hydration was carried out in a flask, which was kept in a constant temperature bath to maintain a specific hydration temperature. The tested hydration temperatures ranged between 5°C and 80°C. The mass ratio of sample to water was 1:20. Water was always in excess, to limit overheating and to ensure that the hydration reaction could proceed to completion. During the hydration process, lasting between 0.5 h and 4 h at each temperature, the sample/water mixture was gently stirred to prevent local overheating and any potential sample agglomeration. After hydration the solids were then filtered off with deionized water and transferred to a vacuum oven maintained at 45°C, to dry for 3-4 h.

Hydration with saturated steam

Steam hydration was conducted in a pressure bomb (Parr Reactor). The sample was loaded in a basket, which was suspended in the middle of the bomb and immersed in the steam. The temperature was controlled at 150°, 200° and 250°C for hydration times between 0.5 and 2 h at each temperature. After steam hydration the solids were dried using the same method as described above.

Re-sulphation

Re-sulphation tests on the hydrated residues were performed in the TGA, again at 850°C for 90 min in simulated flue gas environment. The SO₂ concentration in the simulated flue gas was premixed at 5000 ppmv for sulphating bed ash and fly ash, whereas for sulphating limestone derivatives the SO₂ concentration was 2250 ppmv so that the current results could be compared with the earlier ones produced by other workers at that same concentration [3, 4]. Re-sulphation was also carried out on unhydrated residues as a baseline test to compare with the re-sulphation result of hydrated samples.

Results and discussion

Analysis of original samples

The initial Ca utilization in the received samples was 30% in FA and 43% in BA (Table 1), which are typical of normal sorbent conversions in the CFBC system. The free lime and Ca(OH)₂ content are shown in Table 3. Also, Table 3 shows the back-calculated results for the difference between total CaO and the CaO required for CaSO₄ and CaCO₃ formation. The free lime content in the FA was 26.7% by the sucrose method, which was quite close to the result obtained by back calculation. In the case of the BA, the content obtained by difference was significantly higher than that determined by the sucrose method. This difference was much larger than possible due to experimental errors, indicating that some of the CaO in the BA had combined with fuel ash components, the so-called other calcium compounds (OCCs), e.g., Ca aluminate, silicate, ferrite, and in the case of ash produced from petcoke firing, also vanadates, etc.

Table 3. Free lime and Ca(OH)₂ content in CFBC ash (as wt. CaO%)

	Free lime	Ca(OH) ₂
BA (150-300 microns)	15.4 (29.3 [†])	0.9
FA	26.7 (29.5 [†])	4.5

[†] back calculation from chemical analysis

The most likely explanation for the higher Ca(OH)₂ content in the FA is that the finer particles had a stronger ability to absorb and react with the atmospheric water vapor during storage.

Chemical analysis of the fresh limestones indicated that the CaCO₃ contents in all four samples were similar: 51-54%, as shown in Table 2, while H limestone tends to have more notable dolomitic characteristics with 3% MgO. After overnight-sulphation the conversion of CaO reached about 40% for G, H, C samples and 55% for KR limestone.

Reactivation of CFBC ash

Both steam hydration and liquid water hydration results showed that the free lime could either decrease or increase following hydration. Table 4 shows the results of the free lime after steam hydration. In the case of FA, the free lime content was significantly reduced after 30-min hydration at all steam temperatures when compared with levels prior to hydration. In contrast, for the BA, the free lime appeared to increase to a slightly higher level. This apparently paradoxical result has been previously observed by

Bulewicz *et al.* [5] and was recently confirmed by Wu *et al.* with ashes from the Point Aconi 165 MWe CFBC burning a different coal [6]. Bulewicz *et al.* studied the exothermicity and the free lime level after hydration under pressure for a series of bubbling and circulating FBC ashes and demonstrated that for such ashes the number of moles of Ca present as $[\text{CaO} + \text{Ca(OH)}_2]$ can change. This is regarded as clear evidence that, during the hydration process, free lime can be released from the OCC [2], as well as being consumed by reactions with the coal ash components, such as silica.

Table 4. Free lime and Ca(OH)_2 content in CFBC ash after steam hydration (wt. % CaO)

	Hydration time	Steam temperature					
		150°C		200°C		250°C	
		Free lime	Ca(OH)_2	Free lime	Ca(OH)_2	Free lime	Ca(OH)_2
FA	30 min	20.8±2.3	17.2±0.9	15.4±0.4	9.6±1.8	13.4±1.8	5.8±2.7
	1 h	22.6±2.3	17.8±2.7	14.4	7.9	13.3±1.2	5.7±1.2
	2 h	19.5	14.1	13.7	6.1	13.2	4.7
BA(150-300 microns)	30 min	19.1±4.3	15.1±0.1	18.3±0.9	15.2±0.2	17.6±1.3	15.4±0.8
	1 h	18.5	15.2	18.0	13.9	17.8±0.7	16.2±0.7
	2 h	18.8±1.3	15.5±3.5	16.3±0.8	13.4±2.1	18.7	15.2

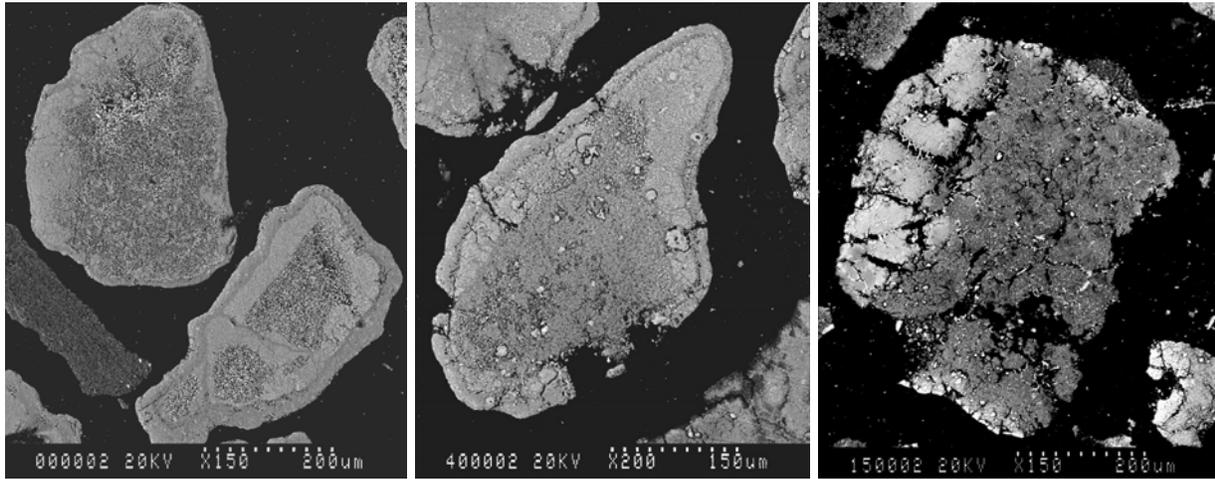
The Ca(OH)_2 content increased rapidly after liquid water hydration for both BA and FA. It was found that Ca(OH)_2 content was higher at higher water temperatures. However, in the case of steam hydration, as shown in Table 4, there was significant difference between FA and BA. For BA, the Ca(OH)_2 content increased quickly after hydration; however, there was little influence of temperature shown in the test between 150°C and 250°C. For FA, Ca(OH)_2 content still increased at the lower temperature of 150°C. As the steam temperature increased, Ca(OH)_2 content decreased steadily. At 250°C, almost no Ca(OH)_2 was present with levels diminished to the initial Ca(OH)_2 content (4.5%) in the FA. Free lime at this temperature must have been consumed by reaction with other components present in the system.

The most significant changes in free lime and Ca(OH)_2 content typically occurred within 30-min hydration in either liquid water or steam. There were only slight fluctuations for longer periods of hydration.

SEM photographs of the unhydrated and hydrated BA (300-600 µm) are shown in Fig. 1. The unhydrated particles (Fig. 1a) appear to have an outer shell or even double shells. The shell was not fully sulphated, consisting of a mixture of CaO and CaSO_4 , while the core was effectively pure CaO. The particles remain whole, showing little sign of being fractured or having started to disintegrate.

The particles hydrated at 40°C for 0.5 hours (Fig. 1b) have a cracked shell and some peripheral disintegration can be clearly seen as a result of the hydration treatment. With hydration at 150°C for 0.5 h, the disruption or disintegration of particles appears to be more advanced. In Fig. 1(c) the sulphate shell around the particle is broken and cracks

are found in the core showing that hydration treatment has affected both the shell and the core at these drastic conditions.



(a) Unhydrated bed ash (b) 40°C water for 0.5 h (c) 150°C steam for 0.5 h
Figure 1. SEM photographs of bed ash (300-600 microns)

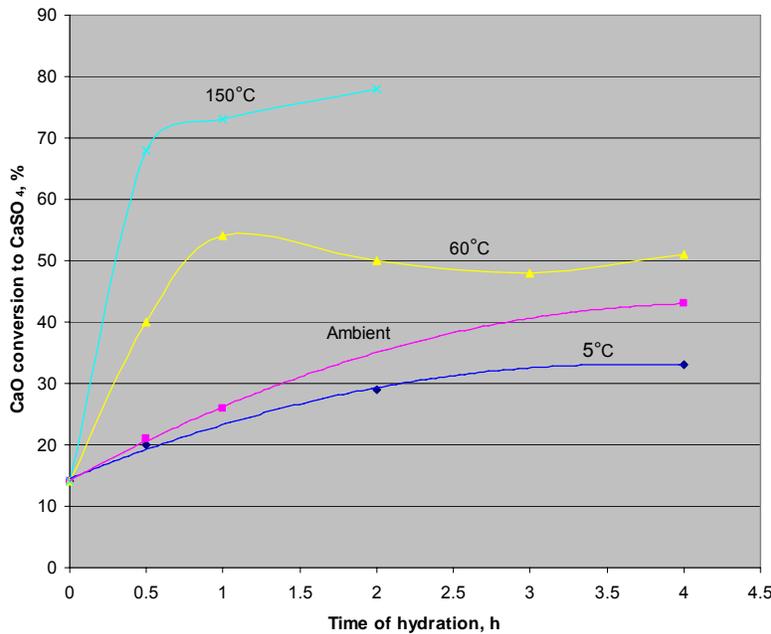


Figure 2. The influence of hydration conditions on re-sulphation (re-sulphation temperature: 850°C, time: 90 min, sample: BA 150-300 microns)

Re-sulphation results for hydrated bed ash are shown in Fig. 2. The samples hydrated at 5°C and at ambient conditions showed clearly increasing trends in conversion with extended hydration time. At 60°C in water and 150°C in steam, however, longer hydration times were less effective in enhancing the SO₂ absorption. For these samples, the most rapid increase in sulphate conversion occurred for hydration durations of 0.5 to 1 h. It can also be seen that the conversion increased with increasing temperature. One

way of explaining these results is to note that hydration for this ash consists of a two-step process, a rapid hydration period which typically finishes in 10 minutes, followed by a much slower process that lasts for hours. For the rapid hydration period, the absolute amount of $\text{Ca}(\text{OH})_2$ produced increases at higher temperatures. In addition, hydration at higher temperature is associated with the development of a much greater degree of fragmentation in the bed ash particles. Therefore, it is easy to envisage, for short-term hydration at low temperatures, not only a lower absolute amount of $\text{Ca}(\text{OH})_2$, but also reduced mechanical damage to the particle sulphate shell due to expansion and dehydration, leading to a correspondingly low reactivation; whereas longer hydration at lower temperature produces more $\text{Ca}(\text{OH})_2$, thus making more calcium available and enhancing ash reactivation. On the other hand, at higher temperatures, since more of the original CaO is already converted to $\text{Ca}(\text{OH})_2$ in the first 30 minutes, longer residence times are subject to the law of diminishing returns and produce only marginal gains.

Fly ash showed distinct sulphation behaviour compared with the BA. The unhydrated FA had a very strong ability to absorb SO_2 , resulting in an apparent remaining CaO conversion greater than 110%. The explanation of these results is provided by the observation in the TGA that, when the fly ash was heated to 850°C in N_2 , a significant weight loss was observed starting from about 820°C . A detailed Fourier Transform Infrared/Thermogravimetric (FTIR/TG) test was conducted on FA holding at 1000°C in helium for 15 min and it was found that 25% of the CaSO_4 decomposed over this period because the char carbon in the original FA acted as a reducing agent. This sulphate decomposition process causes the free lime content of the sample to be grossly underestimated and hence produces utilizations over 100%. In the re-sulphation tests on the FA, the temperature was, therefore, maintained at 850°C in N_2 for about 1 h until completion of this decomposition occurred, before switching to SO_2 for 90-min sulphation. An alternative measure of SO_2 absorption based on mg SO_2 absorbed/g sample was applied for FA to compare the re-sulphation performance, as shown in Table 5.

Table 5. SO_2 absorption capacity of FA after 90 min sulphation, mg SO_2 /g sample

	Unhydrated	Hydration time	Temperature		
			Water		Steam
			Ambient	60°C	200°C
FA	510	30 min	510	467	487
		1 h			430
		2 h			415
		4 h	480	452	

Hydration with either liquid water or steam caused no enhancement of the sulphur capture capability and, if anything, produced a deleterious impact despite the fact that unhydrated FA had the highest ability for SO_2 absorption. The failure of fly ash to respond to reactivation agrees with the observation for bed ash by Laursen *et al.* [3, 4], that the existence of a well-defined core/annulus structure in the sulphated particle is optimal for reactivation. Fly ash particles are generally too small to have the

core/annulus structure. This result also agrees with other earlier work. Couturier *et al.* [7], who studied the reactivation of fly ash with both water and atmospheric pressure steam, failed to find any evidence that fly ash could be reactivated by hydration. Similarly, the work of Schmal [8] showed that filter ash could not be reactivated by hydration, and even earlier work by Argonne National Laboratories also found that, for baghouse ash from the 6' x 6' FBC unit owned and operated by Babcock and Wilcox, fly ash sulphation performance actually deteriorated following hydration treatment [9].

However, it should be noted that fly ash reactivation has been reported several times [10, 11, 12]. In the first two cases the ashes examined came from small pilot-scale rigs, and so this may explain their results (*i.e.*, particles are coarser than fly ash from a full-scale industrial boiler); in the last case, the tests were done in a small industrial boiler, and a possible explanation is that, if the fly ash suffered some agglomeration during the hydration process, its residence time and utilization may have increased even if this ash was not actually reactivated by hydration.

A significant amount of char carbon was observed in the fly ash (Table 1). In order to determine what effect this might have, the fly ash was heated in a crucible to 800°C for 2 h to remove char carbon and the resulting ash was subjected to limited hydration and re-sulphation tests; again this material failed to show any indication that water can reactivate such pretreated ashes.

Fly ash often represents the majority of the solid ash product produced by a CFBC. Further, it will tend to have relatively low sulphation levels given its extremely short residence times in a boiler (typically seconds to minutes). This raises the question as to the strategies available for using it in a reactivation step. It has long been known that, since fly ash is extremely reactive [13], it can be reinjected directly. However, this does not deal with the issue of short residence times. This work clearly shows that hydration with either liquid water or steam is an ineffective strategy. This leaves pelletization of such material as one solution, and early CETC-O work showed that this was an effective, although expensive reactivation method [1]. The benefits of pelletization of fly ash have also been demonstrated at the industrial level [14]. However, there is a new way of carrying out this step, in a cost-effective manner, and this idea has been jointly patented by General Comminution and CETC-O, and demonstrated with a small industrial CFBC boiler at Purdue University [15]. Here, the bed ash is wet ground to accelerate the hydration process to occur in a few minutes. The fly ash (or any other suitable material such as stoker ash) is then mixed into the resulting slurry to produce a dry pelletized material, which is then lightly ground and reintroduced into the boiler. In this way fly ash can be reinjected into the bed in a manner that is likely to increase its residence time without wasting energy by hydrating it.

Reactivation of sulphated limestones

The overall hydration and re-sulphation results for the long-term sulphated limestones are presented in Table 6 and Fig. 3, respectively. For the re-sulphation results of unhydrated residues, the additional conversion of CaO to CaSO₄ ranged from 4 to 6%

(Fig. 3) in 90 min re-sulphation, small enough to suggest that the time for the initial sulphation was sufficient for the fresh limestone to be maximally sulphated.

Table 6. Hydration results for sulphated limestones

Sample	Method of hydration	Hydration time	CaO conversion to Ca(OH) ₂ , wt %	CaO conversion to CaCO ₃ , wt %
CS	-	-	2.9	~0
	Water, 40°C	30 min	77.7	~0
	Water, 40°C	1 h	80.8	~0
	Water, 40°C	4 h	77.5	~0
	Water, 80°C	1 h	81.4	~0
	Steam, 100°C	1 h	83.3	~0
	Steam, 150°C	1 h	80.2	5.1
HS	-	-	5.2	~0
	Water, 40°C	30 min	91	2
	Water, 40°C	1 h	95.7	~0
	Water, 40°C	4 h	88.7	4
	Water, 80°C	1 h	96.3	~0
	Steam, 100°C	1 h	96.1	3.4
	Steam, 150°C	1 h	100	4.5
KRS	-	-	~0	~0
	Water, 40°C	30 min	36.2	~0
	Water, 80°C	30 min	59.4	2.7
	Steam, 150°C	1 h	67.6	4.6
GS	-	-	3.1	0.64
	Water, 40°C	30 min	78.4	2.4
	Water, 80°C	30 min	76.4	1.5
	Steam, 150°C	1 h	72.1	10.5

It should be noted that a small amount of CaO had converted to Ca(OH)₂ in some sulphated samples prior to the hydration. For example, CaO conversion to Ca(OH)₂ for unhydrated GS and CS samples was 3%, and 5% for the HS. This effect was also noticed in previous tests, indicating that these samples have reacted with atmospheric moisture, even though each of them was kept in a capped sample jar. After hydration with either liquid water or steam, CaO conversion to Ca(OH)₂ increased significantly. It reached 70-80% for GS and CS samples. Among the four samples, HS is the easiest one to hydrate with ~100% conversion to Ca(OH)₂ apparently achieved for either liquid water or steam hydration; whereas KRS is most difficult to hydrate, with only 36% of CaO conversion in water hydration at 40°C for 30 min, and a maximum of 67% under more drastic conditions using 1-h steam hydration at 150°C. For the GS, HS and CS samples, CaO conversion to Ca(OH)₂ differed very little for various hydration conditions.

It was also observed that CaO conversion to CaCO₃ after hydration in all four samples was limited to a low level, ranging from 2-5% in most cases. Higher conversion results occurred with steam hydration, which indicated that conversion to CaCO₃ was generally slower or more difficult for water hydration under the conditions employed here.

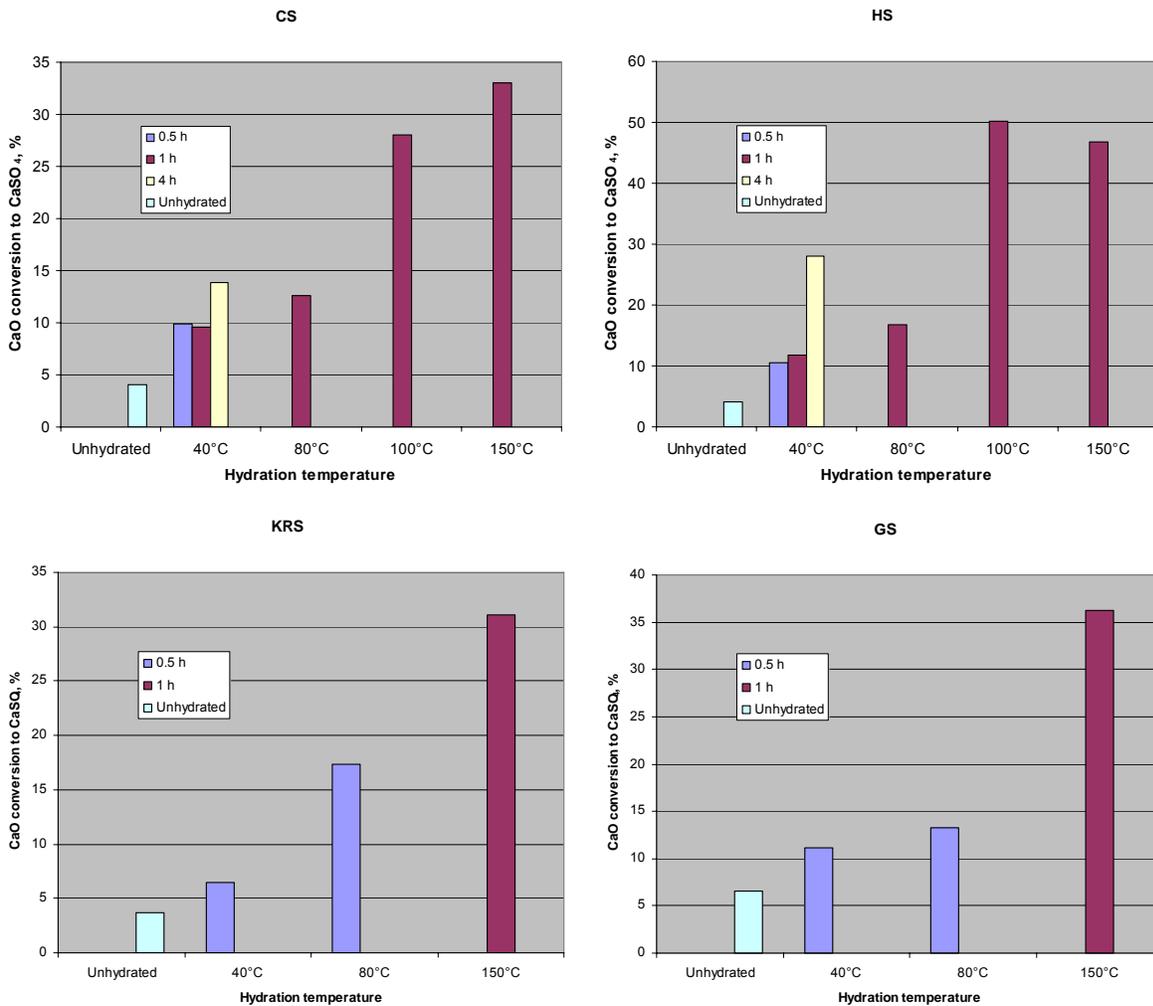


Figure 3. Re-sulphation results of sulphated limestones (re-sulphation temperature: 850°C, time: 90 min)

Re-sulphation results for all water-hydrated samples were similar: the additional CaO conversion to CaSO₄ showed a limited increase following hydration with liquid water. However, in the case of steam hydration the conversion increased significantly to 30–36% for CS, KRS and GS samples. HS again in this work is the easiest to re-sulphate or reactivate after hydration. The additional conversion to CaSO₄ in this sample reached 28% after a longer water-hydration time of 4 h at 40°C. In comparison, this long-term hydration with liquid water did not show substantial improvement for the CS sample—only 14% additional CaO conversion to CaSO₄ was achieved at the same hydration conditions. For the steam-hydrated HS sample, conversion to CaSO₄ increased more significantly to about 50%, which meant that total CaO utilization of 90% was achieved. The fact that the HS sample is easily reactivated with either liquid water or steam might be attributed to its obvious dolomitic properties. However, for both HS and CS samples, increasing steam temperature from 100°C to 150°C failed to produce any more appreciable improvement. The re-sulphation results showed that for all four samples,

hydration with liquid water was notably less effective than with steam for reactivation. It should also be noted that, for a given sample (except KRS) after hydration with either liquid water or steam, no direct correlation was found between the CaO conversion to $\text{Ca}(\text{OH})_2$ and the additional CaO conversion to CaSO_4 .

Cadomin limestone has been classified as being uniformly sulphating in previous studies and Havelock falls in the network/patchy category. It has been suggested that hydration does not reactivate spent sorbents with a uniformly sulphating pattern and shows only a small effect on those which sulphate in a network/patchy pattern [16, 17]. In the work of Laursen *et al.* [3, 17] sulphated Cadomin limestone was not reactivated by hydration. However, the studies on these stones carried out hydration for only short periods, and there is evidence that these limestones were not in fact hydrated [16]. One possible explanation for the failure to reactivate this limestone by previous workers may well be that they chose unsuitable hydration conditions.

Conclusions

A portion of the CaO in the CFBC ash, particularly in the bed ash, had combined with fuel ash components, the so-called other calcium compounds (OCCs). Free lime content in the CFBC ash is not constant following hydration, which provides clear proof that other reactions besides hydration have occurred in the system. The most significant changes of free lime and $\text{Ca}(\text{OH})_2$ content typically take place in the first 30 minutes of hydration.

The CFBC bed ash can be reactivated by either liquid water or steam. For ashes hydrated at ambient or lower temperatures, longer hydration times corresponded to better sulphation performance, while at higher temperatures, longer hydration times produced only marginal effects. The additional CaO conversion increased with increasing hydration temperature at the given hydration time.

The original fly ash contained a significant amount of char carbon and the CaSO_4 decomposed to a large extent in the heating process prior to the re-sulphation. Moreover, there was no significant evidence of reactivation due to any hydration treatment attempted on the fly ash. As fly ash is extremely active, if this ash stream is to be used it might be used directly rather than being hydrated. Pelletization is one of the possible options to re-use the fly ash.

In the case of hydration of sulphated limestones, the unreacted CaO can be quantitatively converted to $\text{Ca}(\text{OH})_2$, whereas the carbonation side reaction was limited. All four limestone samples can be reactivated with either liquid water or steam hydration, although steam hydration was obviously more effective than liquid water in producing reactivation. In earlier work, Cadomin and Havelock limestone have been classified in the uniformly and network/patchy sulphating categories, respectively, and the sulphated Cadomin limestone was demonstrated to not be reactivated by hydration. One of the reasons for the failure to reactivate this limestone by earlier workers might have been an unsuitable choice of hydration conditions.

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