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REACTIVITY OF MARBLE WASTES FOR POTENTIAL UTILIZATION IN WET FLUE GAS DESULPHURIZATION

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Abstract: Wastes of most marble types are distinguished with their superior CaCO_3 content and potential to utilize them as an alternative to limestone. Control of SO_2 using marble wastes in wet flue gas desulphurization (WFGD) units of coal fired thermal power plants is an important opportunity. In this study, nine types of marble wastes were evaluated in terms of their ability to dissolution (reactivity) in an acidic environment. The reactivity was expressed as fractional conversion with time with respect to the chemical composition and particle distribution of wastes as well as temperature and pH of solution. Dissolution reaction rate constants were also computed. Reactivity of the wastes varied significantly with chemical compositions of the marble types. The same marble type displayed different dissolution profiles as a function of test conditions (fineness, temperature, pH). Higher contents of CaCO_3 and Fe_2O_3 positively influenced dissolution ability and rates, whereas increased MgCO_3 content had adverse effects. The changes in particle size, temperature and pH influenced the reactivity. The reactivity increased with decreasing particle size. Also, higher temperature and increased acidity favored dissolution ability of the marble wastes. Our results showed that under optimized conditions marble wastes, having a higher content of CaCO_3 and low content of MgCO_3 , are potential SO_2 sorbent alternative.

Keywords: *marble, reactivity, thermal power production, SO_2 , desulphurization*

Introduction

Coal is the largest fossil fuel resource in the growing energy needs of the globe. Despite the importance of coal fired thermal power plants in power production, it is also the source of major concerns such as SO_2 emission. For SO_2 emission, post-combustion SO_2 capture through wet flue gas desulphurization (WFGD) systems is mostly used (Kaminski, 2003). In these systems, a calcareous sorbent, mainly limestone, put into a slurry form, is used for SO_2 abatement (Zhao et al., 2007). The sorbent particles in the slurry dissolve and react with SO_2 . A dissolution behavior of the calcareous sorbents, i.e. their ability to dissolution determines the extent the sorbent would impose alkalinity and react with the acid generated due to SO_2

dissolution in water (Brown et al., 2010). Susceptibility of the sorbent to dissolution is directly related with the efficiency of desulphurization, the design of the WFGD system as well as the economics and environmental foot print of SO₂ control (Ukawa et al., 1993; Stumpf et al., 1984).

In simulation scale, dissolution of calcareous material in acidic solution resembles the interaction between sorbent and SO₂ in WFGD (Ukawa et al., 1993; Ahlbeck et al., 1995; Hosten and Gulsun, 2004; Siagi and Mbarawa, 2009; Brown et al., 2010). Determination of dissolution ability and dissolution rate of the calcareous sorbent allows an accurate determination of the reactivity of the sorbent and assessment of alternative sorbents for full-scale implementation.

In exploitation of rock blocks, and particularly in marble quarrying, the overall efficiency is extremely low. Geological factors and obstacles, deficiencies during quarrying and processing and technical limitations contribute to generation of massive amounts of marble wastes in various forms. This problem and several associated impacts have been emphasized by several researchers (Davini, 1992; Davini, 2000; Gulsun, 2003; Altun, 2014; Duzyol, 2015). The idea of evaluation of various waste materials as an alternative to limestone, particularly for environmental engineering processes, is not new (Kupich and Girczys, 2008) and use of marble wastes as a limestone supplement could be treated as a similar opportunity. Most marble types can be considered as calcareous stones, not only petrographically, but also on the basis of high CaCO₃ content. At this point the potential of utilization of these wastes arises as an alternative sorbent to limestone in the WFGD systems. Evaluation, particularly the reactivity of marble wastes under different conditions, is a critical aspect to propose such an opportunity. Research on evaluation of marble wastes as a potential SO₂ sorbent is fairly limited except a few studies by Davini (1992 and 2000) and Altun (2014).

This work aims to assess dissolution behavior (reactivity) and reaction rates of marble wastes under various conditions. Wastes of different marble types from the Aegean Region of Turkey were subjected to detailed reactivity investigations. The tests were conducted according to the above mentioned dissolution procedure of wastes under pH controlled conditions. The reactivity of marble waste types were determined with respect to major chemical components and particle size of the wastes, solution temperature and pH.

Materials and methods

Samples and characterization

The study was conducted on nine different marble wastes. The wastes were collected from the major marble quarries in the Aegean Region of Turkey, the leading marble production area of the country. Due to commercial restrictions, names of the marble could not be given and the wastes were coded as Type I to IX (Table 1). The composition characteristics of the wastes were determined using a X-Lab 2000

PED-XRF instrument. For the analysis, representative samples were crushed and ground to a size of $-150\ \mu\text{m}$. Chemical compositions of the marble wastes are presented in Table 1.

Table 1. Chemical compositions of marble wastes

Waste type	Amount (%)					
	CaCO ₃	MgCO ₃	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	K ₂ O
Type I	97.80	1.20	0.66	0.08	0.12	0.10
Type II	96.04	0.81	0.74	0.66	0.78	0.52
Type III	94.12	3.56	1.02	0.48	0.50	0.24
Type IV	94.00	3.60	1.40	0.52	0.40	0.12
Type V	92.56	5.25	1.10	0.38	0.54	0.12
Type VI	89.28	7.12	1.15	0.86	0.98	0.42
Type VII	89.00	7.36	1.62	0.98	0.88	0.14
Type VIII	87.40	11.22	0.66	0.10	0.10	0.10
Type IX	86.10	9.85	0.96	1.52	0.98	0.42

Determination of dissolution behavior

The study is based on quantification of dissolution behavior of calcareous material in an acidic medium, i.e. measurement of the extent of reaction of the calcareous sorbent with a strong acid such as HCl or H₂SO₄. It is well established that the procedure simulates the SO₂ abatement process in wet flue gas desulphurization (WFGD) systems (Hosten and Gulsun, 2004; Siagi and Mbarawa, 2009; Brown et al., 2010). Hence, this application was used as a standardized procedure to measure the reactivity of calcium based sorbents. Here, reactivity corresponds to the dissolution ability of the sorbent.

For identifying the reactivity of calcareous sorbents, a solution was prepared by dissolving the sorbent. The pH of this solution should be kept constant at a designed level. This was achieved by adding HCl in a controlled way. Consumed acid volume with time, stoichiometrically provided the fractional conversion, i.e. the reactivity of the sorbent and by using the reactivity, dissolution rate of the sorbent was calculated. Details of this procedure and the underlying chemical mechanism are described elsewhere (Shih et al., 2000; Gulsun, 2003; Siagi and Mbarawa, 2009; Altun, 2014).

Tests were conducted using a system that included a pH pump, stirred 5 dm³ reactor for sorbent solution, beaker with acid solution, analytical scale and data-logger (Fig. 1). Finely ground marble waste with mass of 4 g was dissolved in 2.5 dm³ of distilled water in the stirred reactor. pH of this solution was maintained at the desired level by the pH pump with automatic titration. The pH pump were transferring required amount of 0.1 M HCl solution when necessary.

Reactivity of the marble wastes were assessed with respect to the chemical composition and particle size of the sorbent, temperature and pH of the sorbent

solution. First of all, the influence of chemical composition on the reactivity was evaluated. Taking into account industrial scale WFGD requirements, the tests were performed with wastes ground to a size of $-45 \mu\text{m}$ and at sorbent solution pH equal to 5.0.

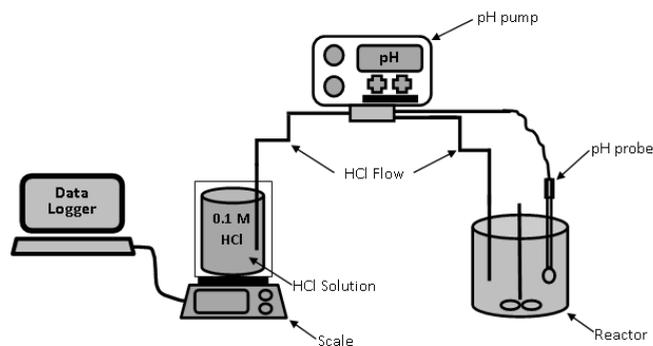


Fig. 1. System for reactivity tests

The tests to determine the effect of sorbent particle size, pH and temperature of the solution were conducted on the marble waste that yielded the highest dissolution ability. For the effect of particle size, reactivity tests on P_{100} sizes of 37, 44, 53, 75 and $100 \mu\text{m}$ were done. For the effect of temperature, reactivity tests at 25, 35, 45 and 55°C were performed. For the effect of pH, reactivity tests on solution pH's of 3.0, 4.0, 5.0, 6.0 and 7.0 were conducted.

In the several previous works, dissolution of calcareous materials has been well explained by the shrinking core model, where the rate of dissolution has been anticipated as being controlled by the surface reaction (Gulsun, 2003; Ahlbeck et al., 1995; Siagi and Mbarawa, 2009; Altun, 2014). This yields the following equation for computing the reaction kinetics of marble waste dissolution in aqueous medium:

$$t = \frac{\rho_k R}{k_S C_A} \left[1 - (1 - X)^{\frac{1}{3}} \right], \quad (1)$$

where t is the reaction time (min), R the universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), X conversion fraction of dissolving material, ρ_k molar density of sorbent (kg mol m^{-3}), C_A concentration of HCl in solution (mol cm^{-3}), k reaction rate constant (min^{-1}). Further simplification of this equation gives:

$$kt = 1 - (1 - X)^{\frac{1}{3}}. \quad (2)$$

After the computation of $1 - (1 - X)^{\frac{1}{3}}$ values and plotting these as a function of time, the slope of obtained curve corresponds to the k value, i.e. the reaction rate constant. Higher k means higher dissolution rate of the sorbent during reactions in WFGD.

Results and discussion

Effect of chemical composition

Marble wastes considered in this work mainly consisted of CaCO_3 and MgCO_3 with lesser contents of SiO_2 , Fe_2O_3 and other minor components (Table 1). The contents of these components varied significantly with respect to the waste type. Type I and II wastes were distinguished with their superior CaCO_3 content, while types VI to IX involved comparatively higher MgCO_3 (Table 1).

Dissolution behaviors of marble wastes expressed as fractional conversion, X (%) as a function of time (minute) are presented in Fig. 2. The reaction rate constants were calculated by using the plot of $1 - (1 - X)^{1/3}$ vs. time for dissolution reaction of each waste type. The fractional conversion for each waste type at certain time (at 15, 30, 50, 70, 100 and 120 minutes) as well as the calculated reaction rate constants are presented in Table 2 with respect to the major components in the wastes.

Table 2. Dissolution characteristics of marble wastes vs. major components (decreasing order)

Waste type	Fractional conversion, X (%)						Reaction rate const., k (min^{-1})	CaCO_3 (%)	MgCO_3 (%)	Fe_2O_3 (%)
	15 min	30 min	50 min	70 min	100 min	120 min				
Type I	42	56	64	70	77	82	$2.9 \cdot 10^{-4}$	97.80	1.20	0.66
Type II	38	53	62	68	76	80	$2.8 \cdot 10^{-4}$	96.04	0.81	0.74
Type IV	32	47	57	63	71	74	$2.6 \cdot 10^{-4}$	94.00	3.60	1.40
Type III	30	44	54	61	70	72	$2.4 \cdot 10^{-4}$	94.12	3.56	1.02
Type V	26	41	51	58	67	68	$2.3 \cdot 10^{-4}$	92.56	5.25	1.10
Type VII	21	36	46	52	63	64	$2.2 \cdot 10^{-4}$	89.00	7.36	1.62
Type VI	20	33	44	53	63	63	$2.0 \cdot 10^{-4}$	89.28	7.12	1.15
Type IX	17	30	40	48	59	59	$1.8 \cdot 10^{-4}$	86.10	9.85	0.96
Type VIII	13	25	35	44	56	57	$1.5 \cdot 10^{-4}$	87.40	11.22	0.66

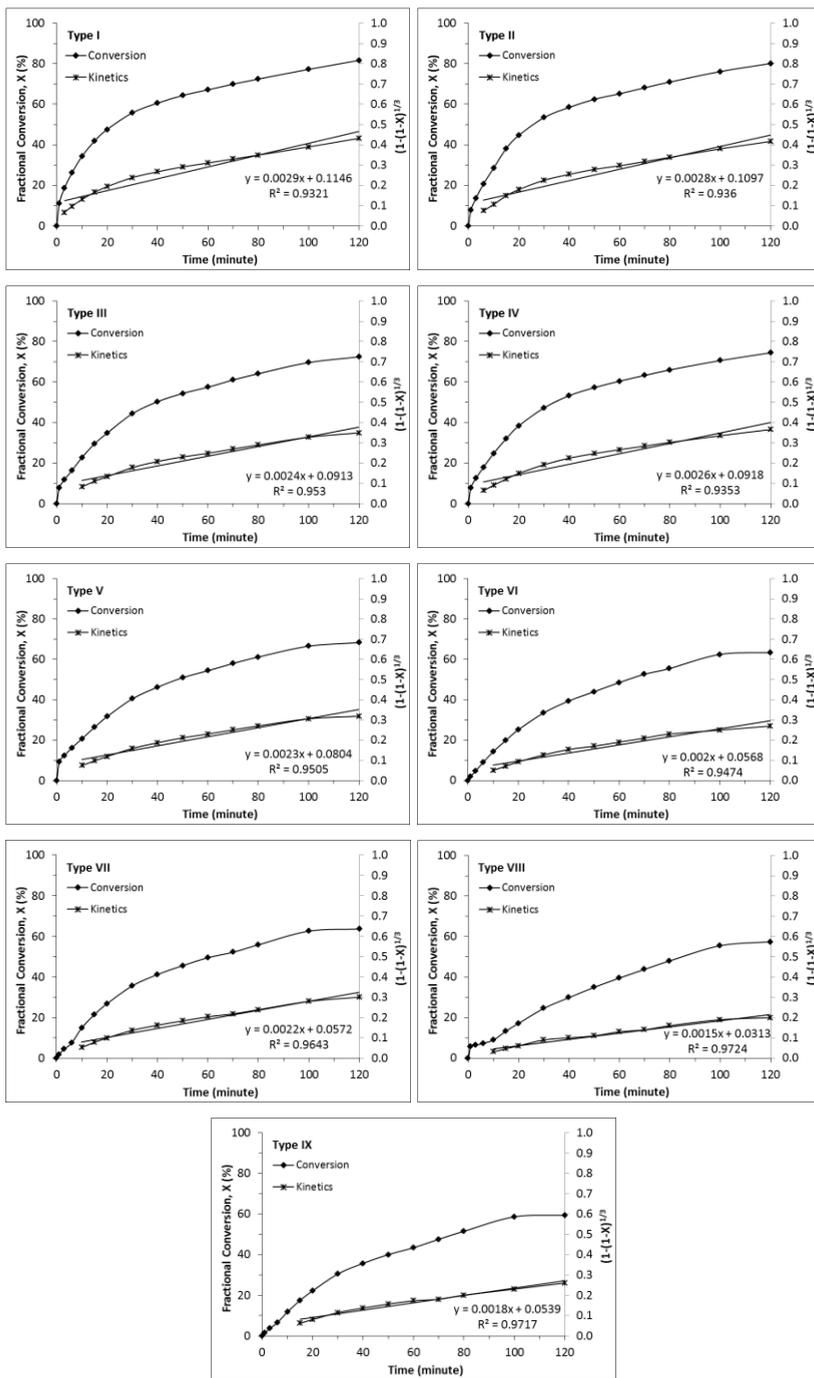


Fig. 2. Dissolution behavior of marble wastes with time

Type I and II wastes provided the highest ability to dissolution after 120 minutes, with fractional conversions of 82 and 80 %, respectively (Table 2). For Types III and IV the best reactivity was equal to 72 and 74%, respectively. For Types V, VI and VII, the ability to dissolution was moderate with the fractional conversions of less than 70% after 120 minutes. For Types VIII and IX the fractional conversions as low as 57 and 59%, respectively were recorded (Fig. 2 and Table 2). The extents of conversion for these two waste types were also low after 15, 30, 50, 70 and 100 minutes (Table 2). In conformity with the dissolution profiles, the waste types with the highest extents of dissolution yielded the highest reaction rate constants (Fig. 2 and Table 2): For Type I and II, k values were $2.9 \cdot 10^{-4}$ and $2.8 \cdot 10^{-4} \text{ min}^{-1}$, respectively, while k was equal to $1.5 \cdot 10^{-4} \text{ min}^{-1}$ for Type VIII waste (Table 2).

The obtained results indicate that despite being calcareous materials, the reactivity of marble wastes may significantly vary. On the basis of the assessment of the changes in the reactivity of wastes and contents of CaCO_3 , MgCO_3 and Fe_2O_3 (Table 2), dissolution behavior of wastes is particularly linked with these three compounds. The abundancy of CaCO_3 is a major aspect that favors the dissolution ability of the sorbents. Type I and II wastes, distinguished with the highest fractional conversion had outstanding extent of CaCO_3 among the wastes studied. Also, with decrease of CaCO_3 down to 87.40% (Type VIII waste), the fractional conversion was as low as 57% (Table 2). The favoring effect of CaCO_3 on the reactivity has been reported in several previous studies on the dissolution behavior of calcareous materials (Hosten and Gulsun, 2004, Lianqing and Jingjuan, 2011; Altun 2014). This effect is due to the abundance of carbonate ions that show the ability to dissolution and affinity to reaction with the hydrogen and/or hydronium ions in acidic solutions (Ahlbeck et al., 1995; Carletti et al., 2012).

It would be misleading to attribute the dissolution ability of wastes only to the content of CaCO_3 . The results also revealed an influence of MgCO_3 on the reactivity. Unlike CaCO_3 , MgCO_3 negatively affected dissolution of the wastes. In addition to the reactivity, a low content of CaCO_3 in Types VIII and IX having apparently higher MgCO_3 (11.22 and 9.85%, respectively), should contribute to a low reactivity of these sorbents. Another observation which supports this is the dissolution behavior of marble wastes having similar content of CaCO_3 but varying amounts of MgCO_3 . Type I-II and type VIII- IX illustrate this case. Type II reveals almost an equivalent ability to dissolution to type I waste, despite 2% lower CaCO_3 content. Also, although CaCO_3 content of type VIII waste is higher than that of type IX, type IX, it yields higher fractional conversion and greater reaction rate constant (Fig. 2 and Table 2). It is attributed to the higher MgCO_3 contents of type I and VIII wastes. The inhibiting influence of Mg on reactivity of calcareous sorbents has been reported by other researchers (Ahlbeck et al., 1995; Hosten and Gulsun, 2004; Siagi and Mbarawa, 2009; Lianqing and Jingjuan, 2011; Carletti et al., 2012; Altun, 2014) and is attributed to the lower dissolution rate of dolomite as compared to that of calcite (Lund et al., 1973; Lianqing and Jingjuan, 2011).

The effect of Fe_2O_3 on the dissolution behavior should also be noted. For sorbents with similar CaCO_3 and MgCO_3 contents, as in the cases of type III- IV and type VI-VII couples, the ability to dissolution is influenced by the content of Fe_2O_3 . A higher Fe_2O_3 content favors dissolution and reaction rate: type IV marble waste yields a higher fractional conversion and a greater reaction rate constant as compared to type III. The content of Fe_2O_3 of type IV (1.40 %) is higher than that of type III waste (1.02 % Fe_2O_3). Similar results were attained for the type VI-VII pair. The higher content of Fe_2O_3 in type VII (1.62 %) provided higher dissolution ability and faster dissolution as compared to the type VI waste (1.15 % Fe_2O_3), although these two waste types had similar contents of CaCO_3 and MgCO_3 (Fig. 2 and Table 2). It confirms the previous findings. The presence of iron was reported to increase the dissolution rate of calcareous sorbents as well as their SO_2 capture performance (Davini, 2000; Lianqing and Yin, 2011), and it was associated with the catalytic activity provided by iron over dissolution of sorbent particles.

Type I and II wastes were identified to provide the distinctive dissolution behavior and the highest reactivity as compared to other waste types. Subsequently further research was conducted using the Type I waste.

Effect of particle size

The particle distribution of the sorbent is another major aspect to attain sufficient SO_2 control performance in WFGD units. Limestone, the common sorbent in WFGD units, is used in powder form, and therefore it has to be intensively ground to the required particle size. The commonly applied particle size in WFGD is 100% passing (P_{100}) 45 μm . This is achieved by crushing the limestone in a ball milling. In general, reducing the sorbent to the required fine particle sizes is not a problem, but comminution and particularly grinding is a highly energy-consuming and an expensive process.

The influence of the particle size on the reactivity is investigated to identify the changes in the dissolution behavior of marble wastes with respect to the particle size. The opportunity of using coarser particles for comparable reactivity to the commonly used P_{100} size of 45 μm was also investigated. The dissolution behaviors of type I wastes ground to P_{100} sizes of 37, 44, 53, 75 and 100 μm are shown in Fig. 3. The fractional conversions after 15, 30, 50, 70, 100 and 120 minutes and the reaction rate constants corresponding to different P_{100} sizes are also presented in Table 3.

Table 3. Dissolution characteristics of Type I marble waste as a function of particle size

P_{100} (μm)	Fractional conversion, X (%)						Reaction rate const., k (min^{-1})
	15 min	30 min	50 min	70 min	100 min	120 min	
37	45	59	67	72	79	84	$3.0 \cdot 10^{-4}$
44	42	56	64	70	77	82	$2.9 \cdot 10^{-4}$
53	39	54	63	69	76	80	$2.9 \cdot 10^{-4}$
75	35	49	60	66	73	74	$2.6 \cdot 10^{-4}$
100	31	44	55	62	68	68	$2.4 \cdot 10^{-4}$

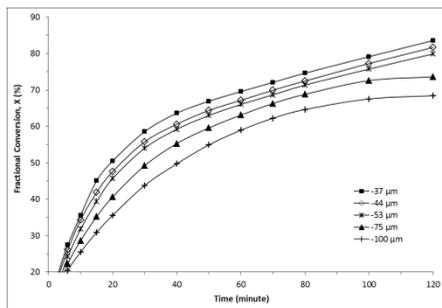


Fig. 3. Dissolution behavior of Type I marble waste with respect to particle size

The results showed that particle size of the sorbent is a critical aspect that remarkably affects the reactivity. Firstly, it should be noted that P_{100} size of 53 μm is a critical point for sorbent fineness and decrease down to 44 μm and further reduction to 37 μm provided slight increases in the fractional conversion values (Fig. 3 and Table 3). At P_{100} size of 53 μm , the fractional conversion after 120 minutes was 80% and gradually increased to 82 and 84% at P_{100} sizes of 44 and 37 μm , respectively. Although 4% difference in the fractional conversion might seem apparent, size reduction to 37 μm rather than 53 μm is a critical trade-off due to the energy-intensive nature of grinding. It should also be noted that the same reaction rate constant value ($2.9 \cdot 10^{-4} \text{ min}^{-1}$) was achieved for dissolution of 53 and 44 μm and it increased only to $3.0 \cdot 10^{-4} \text{ min}^{-1}$ at the extreme fineness of 37 μm (Table 3). This implies that the reactivity of the 53, 44 and 37 μm sizes were slightly different.

Using coarser particles reduced the reactivity of type I marble waste. For particle size of 75 μm , fractional conversions were apparently lower at time as compared to 53 μm and after 120 minutes it was as low as 74% (Fig. 3 and Table 3). For particles 100 μm , the reactivity of the sorbent was quite low, yielding dramatically reduced fractional conversions at all instants. Only 68% fractional conversion was attained after 120 minutes. Relatively lower reactivity of the coarsest particles was also reflected with the lowest reaction rate constant of $2.4 \cdot 10^{-4} \text{ min}^{-1}$ (Table 3).

These results showed that the amount of marble waste converted for the same time periods became higher with increase in fineness. These observations are in agreement with the previous statements on the dissolution-particle size relation of other calcareous sorbents (Hosten and Gulsun, 2004; Siagi and Mbarawa, 2009). The increase in the reactivity of finer particle sizes was attributed to the increase in the surface areas of the sorbent entities, leading to relatively faster dissolution and higher fractional conversions, particularly at the initial phases of reaction.

Effect of temperature

The effect of temperature on the dissolution behavior of marble wastes is shown in Fig. 4. Also, the fractional conversions at time and the reaction rate constants computed at different temperatures are presented in Table 4.

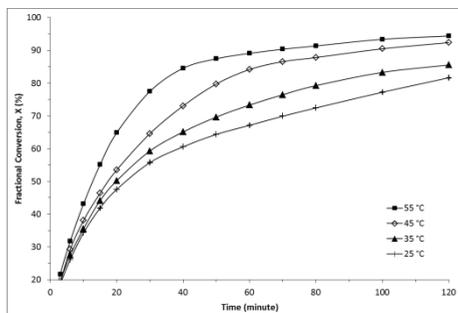


Fig. 4. Dissolution behavior of Type I marble waste with respect to temperature

Table 4. Dissolution characteristics of Type I marble waste as a function of temperature

Temperature (°C)	Fractional conversion, X (%)						Reaction rate constant, k (min^{-1})
	15 min	30 min	50 min	70 min	100 min	120 min	
25	42	56	64	70	77	82	$2.9 \cdot 10^{-4}$
35	44	59	70	76	83	86	$3.4 \cdot 10^{-4}$
45	46	65	80	87	90	92	$4.5 \cdot 10^{-4}$
55	55	77	87	90	93	94	$4.6 \cdot 10^{-4}$

At temperatures from 25 to 55 °C the reactivity of marble wastes increased gradually and fractional conversion values became higher with temperature. For instance, the fractional conversion of 70% at 25 °C increased to 90% at 55 °C. After 120 minutes, the fractional conversion of 82% at 25 °C was as high as 94% at 55 °C (Table 4). The effect of temperature on dissolution of wastes was clearly seen in dissolution vs. time profiles (Fig. 4). With increase in temperature, dissolution of wastes occurred much faster (the fractional conversion that approximated to the highest conversion value recorded at the 120th minute was achieved earlier). At temperatures from 45 and 55 °C the fractional conversion equal to 87% was achieved only after 50 and 70 minutes, respectively, and 87% of the fractional conversion was higher than the fractional conversion after 120 minutes at 25 (82%) and at 35 °C (86%) (Table 4). Higher reactivity and increased rates of dissolution with increases in temperature were clearly reflected by the reaction rate constants. As the temperature shifted from 25 to 55 °C, the reaction rate constants increased. The reaction rate constant of $2.9 \cdot 10^{-4} \text{ min}^{-1}$ at 25 °C raised to $4.6 \cdot 10^{-4} \text{ min}^{-1}$ at 55 °C. The reaction rate

constant increased from $3.4 \cdot 10^{-4}$ to $4.5 \cdot 10^{-4} \text{ min}^{-1}$ when the temperature increased from 35 to 45 °C (Table 4).

The obtained results indicated the favoring influence of temperature on the reactivity of marble wastes. With gradual increments in temperature, dissolution of the wastes occurred more effectively. Not only the ability to dissolution, but also the rate of dissolution was positively affected, with remarkable increases in reaction rates observed particularly at 45 and 55 °C. Here, dissolution temperature of 45 °C would be noted as the optimum level. The increase in fractional conversion values and reaction rate constants from 35 to 45 °C was observed. However the dissolution profiles and reactivity indicators at 45 and 55 °C were slightly different (Fig. 4 and Table 4).

Effect of pH

The effect of pH on dissolution profiles of marble wastes is shown in Fig. 5. Changes in the fractional conversions and reaction rate constants as a function of solution pH are presented in Table 5. The pH was quite influential on the reactivity and the changes in dissolution ability and reaction kinetics were apparent when the pH of the solution was shifted from acidic to neutral. The fractional conversions became gradually less at time as the solution was less acidic. The fractional conversion of 85% at the 120th minute at pH 3.0 dropped by 20% at neutral pH (Table 5). The reaction tended to occur more slowly with pH increase, as revealed by the decrease in the reaction rate constant, particularly above pH 5.0. The reaction rate constant decreased from $3.2 \cdot 10^{-4}$ to $2.2 \cdot 10^{-4} \text{ min}^{-1}$ as the solution pH increased from 3.0 to 7.0 (Table 5). It should be noted that despite the decreasing trend, reductions in the fractional conversion values and reaction rate constants were relatively slight as the pH of the solution increased from 3.0 to 4.0, and then to 5.0. However, above pH 5.0, the negative influence of decreasing acidity on reactivity was apparently observed (Table 5).

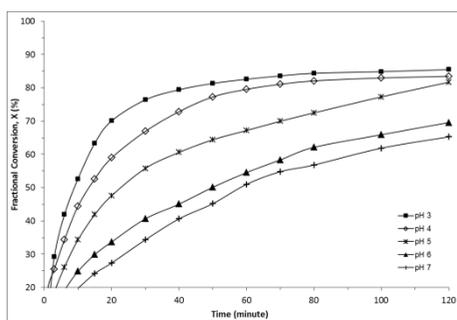


Fig. 5. Dissolution behavior of type I marble waste with respect to pH

Table 5. Dissolution characteristics of Type I marble waste with respect to pH

pH	Fractional conversion, X (%)						Reaction rate constant, k (min^{-1})
	15 min	30 min	50 min	70 min	100 min	120 min	
3.0	63	76	81	84	85	85	$3.2 \cdot 10^{-4}$
4.0	53	67	77	81	83	83	$3.0 \cdot 10^{-4}$
5.0	42	56	64	70	77	82	$2.9 \cdot 10^{-4}$
6.0	30	41	50	58	66	70	$2.4 \cdot 10^{-4}$
7.0	24	34	45	55	62	65	$2.2 \cdot 10^{-4}$

The dissolution ability and reaction rate of marble waste were positively affected by low pH of solution. Considering that the marble waste is a calcareous material, this result was anticipated. As it was suggested by Shih et al. (2000) and confirmed by Siagi and Mbarawa (2009), in dissolution of calcareous sorbents, mass transfer of hydrogen ions is the rate controlling mechanism. As the solution is more acidic, the increase in hydrogen ions causes faster dissolution of calcareous particles. This suggestion also complies with the Ahlbeck et al. (1995) explanation about the interaction of hydronium and carbonate ions during the dissolution of limestone in acidic solution. The findings in this work as well as previous statements imply that, acidic solution pH should be provided in practice, to contribute to the dissolution of marble waste and other potential calcareous sorbents. However, similar to the effect of temperature, a critical level of acidity was observed, which is pH 5.0. Despite the increase in the reactivity and reaction rate of the marble waste below this pH, the changes were not significant. Considering process chemistry and economics, pH 5.0 was proposed as the optimum acidity for a favorable dissolution behavior.

Conclusions

Reactivity, an important aspect for calcareous materials for use as SO_2 sorbent in wet flue gas desulphurization, was assessed for marble wastes. The goal was to identify parameters significantly effecting the dissolution ability of marble wastes. Monitoring fractional conversions with time as a function of chemical compositions of the waste types revealed that CaCO_3 and MgCO_3 mainly determine dissolution characteristics, the latter having a negative factor on reactivity. Fe_2O_3 also influences the reactivity, most probably as a catalyst. Increases in Fe_2O_3 content accelerate dissolution and result in higher dissolution. Fineness was identified as a critical physical sorbent feature. Up to a certain degree of fineness, P_{100} size of $53 \mu\text{m}$ in this work, dissolution profile and ability were remarkably favored. Temperature and pH were also notably effective and the shifts towards higher dissolution temperatures and lower pH conditions, particularly from 25 to 45°C and from pH 7.0 to 5.0, increases reactivity and reaction rates and earlier conversion of the sorbent. However, the degree of particles fineness, temperature and solution pH are the

critical parameters to be considered. Optimization is necessary for implementing marble waste utilization in wet flue gas desulphurization because these three parameters are the major economic and environmental factors of SO₂ control.

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