Marble Wastes as a Calcareous Sorbent for SO₂ Control in Thermal Power Plants

N. Emre Altun
Middle East Technical University, Mining Engineering Department
Ankara, Turkey
ealtun@metu.edu.tr

Abstract - In this study, the possibility of using marble wastes for SO₂ control in coal-fired thermal power plants was assessed. The goal is suggesting marble wastes as an altarnative calcareous sorbent to limestones for use in WFGD systems. Chemical compositions, specific surface areas, grindabilities, reactivities and SO₂ capture capabilities of different marble wastes were identified and compared with three different limestones that are currently in use in thermal power plants. Marble wastes had higher or comparable CaCO₃ and varying extents of MgCO₃ Both limestones and marble mastes were characterized as low-surface area sorbents with similar specific surface area values. Marble wastes generally showed higher liability to size reduction, suggesting an important advantage regarding the energy consumption in the sorbent preparation phase. Reactivity of the sorbents were highly sorbent specific. Some waste types showed higher or comparable dissolution rates as compared to the limestones while some resulted in a relatively slower dissolution. Calcite and dolomite contents dictate reactivities and an increase in MgCO₃ adversely affect liability of the sorbent to dissolution. Assessment of the gas emission profiles during combustion by EGA-FTIR also pointed to better or comparable SO₂ capture for some marble waste types in comparison with limestones. SO₂ control was linked with the extent of calcite in the sorbents. Overall, findings suggest that an opportunity exists for utilizing marble wastes as an alternative to limestone in WFGD, provided that the key sorbent features and requirements are assessed and justified.

Keywords: Marble waste, limestone, SO₂ control, reactivity, waste utilization.

1. Introduction

Coal is a major energy resource and power production in coal-fired thermal power plants still have a significant share in meeting energy needs of the globe [1-3] despite serious environmental concerns associated with coal utilization. Post-combustion sulphur dioxide (SO₂) emissions remain to be an issue related with coal-fired thermal power plants and effective SO2 control is a critical matter to be addressed for sustainable thermal-power production. In these plants, post-combustion desulphurization is the most common method for SO₂ control [4] and in more than 80% of the desulphurization systems in the globe, wet flue gas desulphurization (WFGD) is used. In WFGD systems a finely-ground, calcium-based material (commonly limestone) is utilized as the SO₂ sorbent [4].

The total efficiency in the production of dimension stones (from quarrying to the final product) is ≈10 %. This fairly low efficiency results in huge amounts of stone wastes. Marble is, the most important type of dimension stone based on the production and consumption figures globally. In the leading marble producing countries, marble wastes are generated in many different forms. Marble wastes are encountered as an environmental problem as well as economic losses. The use of marble wastes as an alternative sorbent for SO₂ control in the WFGD systems might be an important opportunity. Nevertheless, a systematic assessment of this opportunity and comparison of marble wastes with limestones is highly lacking except Davini's work limited to some marble wastes from Italy [5-6]. Various physical and chemical features should be assessed to assess possible utilization of marble wastes in WFGD systems.

The objective of this work is to investigate the possibility for utilization of marble wastes for SO₂ control as an alternative calcareous sorbent. In this context, different types of marble wastes were assessed and compared with limestones w.r.t critical aspects and sorbent features.

2. Materials and Methods

Five different marble wastes and three different limestones were used in this work. The wastes are from the south-west Aegean region of Turkey, a major marble-production area. Limestones are obtained from three different thermal power plants in the same region, and are actively being used as calcareous sorbents in the WFGD systems. Chemical compositions of the sorbents were determined by XRF. Specific surface areas of the samples were determined using a Micromeritics ASAP 2020 – BET instrument. The grindability of the marble wastes and limestones were determined through the standard Bond Grindability Test and the specific Bond Work Index value was identified for each sample [7]. The liability of the marble wastes and limestones to dissolution, i.e. the reactivities were determined using the setup shown in Fig. 1. The setup consists of a pH pump for acid titration, a reactor with the sorbent solution, a beaker with acid solution, a scale and a data logger. The details of the ''reactivity measurement'' procedure is described elsewhere [8]. The amount of acid consumed for a given period corresponds to the reactivity of the sorbent, i.e. higher acid consumption corresponds to higher sorbent liability to dissolution, thereby a favorable reactivity within the WFGD system for controlling SO_2. The effectiveness of marble wastes and limestones for SO_2 control were also identified through Evolved Gas Analysis (EGA) using a Perkin Elmer TG7 thermal analyzer coupled with a Perkin Elmer 2000 FTIR. For EGA, calcined marble wastes and limestones were mixed with ROM coal at 10% by wt. Absorbance intensities of SO_2 emission bands on the FTIR spectra of the run-of-mine (ROM) coal and sorbent added coal were obtained and used for qualitative comparison of the performance of sorbents in controlling SO_2. Approximately 25 mg of sorbent added coal samples were combusted at a heating rate of 10 ^{0}C/min from ambient to 900 ^{0}C with an airflow of 50 ml/min. The spectral range in FTIR analysis was 400 cm^{-1} – 4000 cm^{-1}, providing the 3-D emission profiles of the evolved gases as a result of combustion.
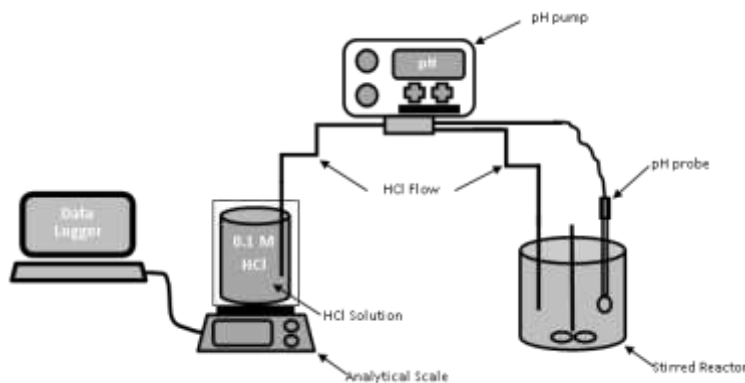

Fig. 1: Setup for determining sorbent reactivity.

3. Results and Discussion

3.1. Comparison of Compositional Characteristics of the Sorbents

Chemical compositions of limestones and marble wastes are shown in Table 1. All limestones are high-calcium sorbents. Yatağan limestone has higher dolomitic content in comparison with other limestones. Some marble wastes had higher while some had lower calcite and dolomitic contents compared to limestones. C-MW marble waste is distinguished with a high calcite (98.92 %) and low dolomitic content (0.45 %) among all sorbents. Relatively low calcite (87.7 %) and high dolomite (10.15 %) in T-MW2 marble waste should be noted. All marble wastes had lower SiO_2 than limestones (Table 1). It is known that, higher calcite content of the sorbent is critical for effective SO_2 control in WFGD systems. Yet, dolomitic content may adversely affect SO_2 control: Magnesium may hinder the reactions among the sorbent and SO_2 [8-12]. Thus, Yatağan limestone may provide lower SO_2 capture due to its higher dolomitic content (1.72 %) than the other two limestones. This also applies for the marble wastes; C-MW and T-MW1 marble wastes would be favorable for SO_2 capture, with their high calcite and limited dolomitic contents. PK-MW, T-MW3 and particularly T-MW2 marble wastes, however, might provide lower SO_2 capture, due to higher $MgCO_3$ contents.

Table 1: Chemical compositions of sorbents.

Sample		CaCO$_3$	MgCO$_3$	SiO$_2$	NaO	Fe$_2$O$_3$	Al$_2$O$_3$	K$_2$O	TiO$_2$	P$_2$O$_5$	SO$_3$	Cl
						Amount (%)						
Limestone	Yatağan	95.29	1.72	1.54	0.04	0.38	0.75	0.12	0.05	0.01	0.07	0.01
Limestone	Yeniköy	97.10	0.41	1.29	0.05	0.37	0.61	0.08	0.04	0.01	0.03	0.01
Limestone	Kemerköy	98.45	0.37	0.54	0.02	0.38	0.14	0.02	-	0.01	0.02	0.02
Marble Waste	PK-MW	94.47	3.51	0.50	0.04	0.84	0.43	0.06	0.05	0.01	0.08	0.01
Marble Waste	T-MW1	98.79	0.9	0.06	0.01	0.13	0.03	0.00	-	0.05	0.02	0.01
Marble Waste	T-MW2	87.70	10.15	0.42	0.02	1.42	0.22	0.01	-	0.02	0.03	0.01
Marble Waste	T-MW3	95.46	4.17	0.06	-	0.22	0.04	0.00	-	0.02	0.01	0.01
Marble Waste	C-MW	98.92	0.45	0.11	0.02	0.34	0.08	0.00	0.03	0.00	0.03	0.01

3.2. Comparison of Key Physical Features of the Sorbents

Table 2 presents the BET specific surface areas of the sorbents. Surface areas varied in a range of 1.66 – 1.95 m^2/g for limestones and 1.03 m^2/g – 2.26 m^2/g for marble wastes, corresponding to ''low porosity'' character for both groups. Briefly, marble wastes had similar or better surface areas than limestones, supporting their potential use in WFGD. Bond Work Indices, indicating the liability of the sorbents to comminution are shown in Table 2. Grindability is critical due to fine-grinding requirements for the sorbents (P$_{90}$ 45 microns) to be used in the WFGD systems. Kemerköy limestone had the highest BWI (12.28 kWh/t) in the limestone group. C-MW marble waste (11.03 kWh/t) also had a lower grindability. All other sorbents showed moderate to low BWI's (<10 kWh/t), an indication of good liability to size reduction. In general marble wastes had favorable grinding characteristics with lower or comparable BWI values as compared to the limestones (Table 3). This implies that use of marble wastes in WFGD systems could reduce energy requirements in the sorbent preparation phase. Other associated advantages include reduced grinding costs, reduced environmental footprint and contributions to the sustainability of the overall operation.

Table 2: Key physical characteristics of the sorbents.

	Limestone			Marble Waste				
	Yatağan	Yeniköy	Kemerköy	PK-MW	T-MW1	T-MW2	T-MW3	C-MW
Sp.Surf.Area (m^2/g)	1.66	1.92	1.95	2.26	2.06	1.03	2.14	2.14
BWI (kWh/t)	9.78	11.33	12.28	8.69	9.76	9.33	9.33	11.03

3.3. Dissolution Behavior of the Sorbents

In WFGD, the calcareous sorbent should be sufficiently reactive to convert into calcium sulphate for capturing SO$_2$ [6,9]. The liability to dissolution, i.e. reactivity, is therefore, an important sorbent selection criteria [9,13]. A good reactivity corresponds to effective SO$_2$ control and reduced sorbent consumption. In this work, sorbent reactivity is expressed as conversion profiles, i.e. the dissolution rates, in an acidic solution within a certain period. Fractional conversions of limestone and marble wastes at specific instants are compared in Table 3. Fig. 2 also illustrates the comparison of complete dissolution profiles for selected limestones and marble wastes.

Kemerköy limestone yielded the highest dissolution among the limestones (51% and 90% conv. after 15 and 120 mins.) while Yatağan limestone yielded the lowest rate of dissolution (Table 3). Among marble wastes, C-MW provided the highest dissolution (91% conv. after 120 mins.). T-MW2 marble waste showed a slower dissolution as compared to other wastes (61% conv. after 120 mins.). C-MW and T-MW1 are highly-reactive marble wastes while T-MW2 shows poor reactivity.

Table 3: Fractional Conversions and Reaction Rate Constants of Sorbents vs. $CaCO_3$ and $MgCO_3$ contents.

| Sorbent		Conversion, X (%)					Reaction Rate Constant (min^{-1})	$CaCO_3$ (%)	$MgCO_3$ (%)
		15th min	30th min	60th min	100th min	120th min			
C-MW	*Waste*	53	65	78	89	91	32 x 10^{-4}	98.92	0.45
Kemerköy	*Limestone*	51	63	76	86	90	31 x 10^{-4}	98.45	0.37
Yeniköy	*Limestone*	50	61	73	84	88	29 x 10^{-4}	97.10	0.41
T-MW1	*Waste*	46	59	71	82	85	28 x 10^{-4}	98.79	0.90
Yatağan	*Limestone*	41	53	65	76	79	24 x 10^{-4}	95.29	1.72
PK-MW	*Waste*	32	45	59	69	72	22 x 10^{-4}	94.47	3.51
T-MW3	*Waste*	30	42	56	67	70	22 x 10^{-4}	95.46	4.17
T-MW2	*Waste*	21	33	47	58	61	19 x 10^{-4}	87.70	10.15
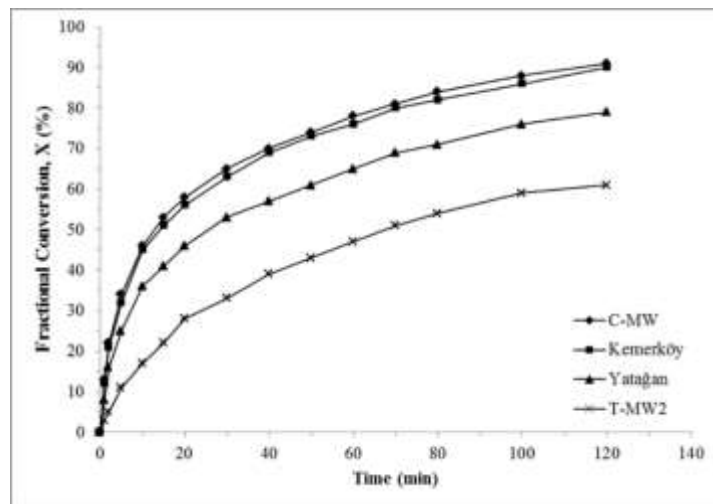
Fig. 2: Fractional conversion profiles of selected limestones and marble wastes.

C-MW also had a higher reactivity than limestones (Table 3 & Fig. 2). Yatağan limestone, PK-MW, T-MW3 and T-MW2 marble wastes seem less favorable for WFGD, with their slower dissolution rates and limited conversions. Reaction rate constant also indicates how fast a sorbent is dissolved [14,15] and are computed by a plot of the dissolution kinetics vs. time. Calculated reaction rate constants for sorbents are presented in Table 3. Reaction rate constant values validate dissolution characteristics of the sorbents. C-MW marble waste and Kemerköy limestones, i.e. highly-reactive sorbents, had the highest reaction rate constants. Poor reactivity of T-MW2 was justified with the lowest reaction rate constant.

An assessment of the compositional features and reactivities of the sorbents suggests that $CaCO_3$, $MgCO_3$ contents and conversion extents were correlated. C-MW marble waste showed the highest reactivity and had the highest calcite (98.92%). The least reactive T-MW2 marble waste had the lowest calcite (87.70%). In general, an increase in calcite positively influences sorbent's reactivity (Table 3), however, the link between $MgCO_3$ content and dissolution was more significant. Dolomite adversely affected dissolution of the sorbents. The highly-reactive sorbents, C-MW marble waste, Kemerköy and Yeniköy limestones had limited $MgCO_3$ (0.37 – 0.45%) while T-MW2 marble waste is distinguished with the highest $MgCO_3$ (10.15%). An increase in $MgCO_3$ leads to reduced fractional conversion. For sorbents with similar calcite contents, the difference in reactivities arises due to the difference in dolomitic contents. A comparison of the T-MW1 marble waste vs. Yeniköy limestone and/or T-MW3 vs. PK-MW marble wastes justifies this postulation. The positive influence of calcite and the negative influence of dolomite on reactivity were reported previously [8,14,16].

3.4. SO₂ Control Capability of the Sorbents

To identify the effectiveness of SO_2 control using limestone and marble wastes as sorbents, effluent gas analysis (EGA) was undertaken. EGA-FTIR spectra shows the emitted gases with corresponding temperatures of evolution over the combustion of ROM- and sorbent added coal. Fig. 3 presents the EGA-FTIR spectra of the ROM coal with the characteristic bands of major emissions: The band at 1202-1466 cm^{-1} corresponds to SO_2 emission, the major focus in this work. Peak absorption intensities for SO_2 emissions, extracted from the entire FTIR spectra, are presented in Table 4 with respect to the sorbent type.
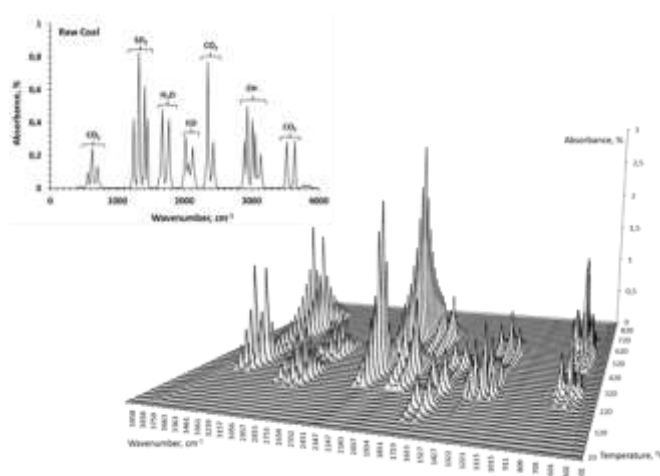

Fig. 3: Bands of emitted gases at 260 ^{0}C (above) and complete EGA profile of ROM coal.

Table 4: SO₂ emissions relative peak intensities for different sorbents.

Peak Temp.	Absorbance cm^{-1}								
	Raw Coal	Kemerkoy LS	C-MW	T-MW1	Yenikoy LS	Yatagan LS	PK-MW	T-MW3	T-MW2
260 ^{O}C	0.826	0.118	0.121	0.129	0.135	0.179	0.188	0.271	0.367
320 ^{O}C	0.552	0.078	0.080	0.086	0.090	0.119	0.149	0.170	0.263
520 ^{O}C	0.607	0.086	0.089	0.095	0.100	0.134	0.168	0.190	0.296

In view of the spectrum, SO_2 evolution is observed in the temperature range of 220-600 ^{O}C. Within this range three major emission peaks (at 260 ^{O}C, 320 ^{O}C, 520 ^{O}C) were recorded. The band of SO_2 emission peaks at 260 ^{O}C were compared in Fig. 4. SO_2 absorption bands are clearly reduced after the sorbent addition and the extent of reduction, depends on the sorbent type. Kemerköy provides the highest reduction in SO_2 emissions in the limestones group. In marble wastes C-MW is an

effective sorbent and leads to the highest reduction in the SO_2 peak intensities. Its effectiveness in SO_2 control is comparable with Kemerköy limestone. Use of T-MW1 marble waste also yields similar SO_2 emission profile with C-MW waste and Kemerköy limestone (Fig. 4). Use of T-MW1 provides lower SO_2 emission intensities than Yeniköy and Yatağan limestones. T-MW3 and T-MW2 marble wastes also resulted in notable reductions in SO_2 peak intensities, but, at relatively lower extents.
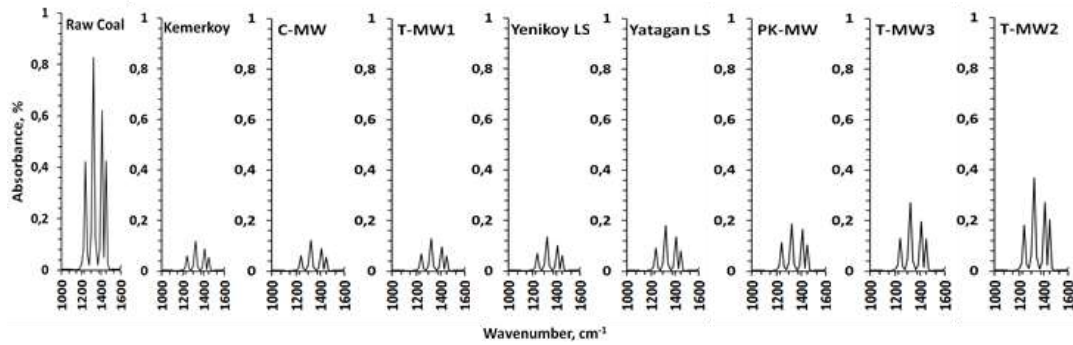
Fig. 4: SO_2 Emission intensites of ROM- and sorbent added coal samples at 260 ^{0}C.
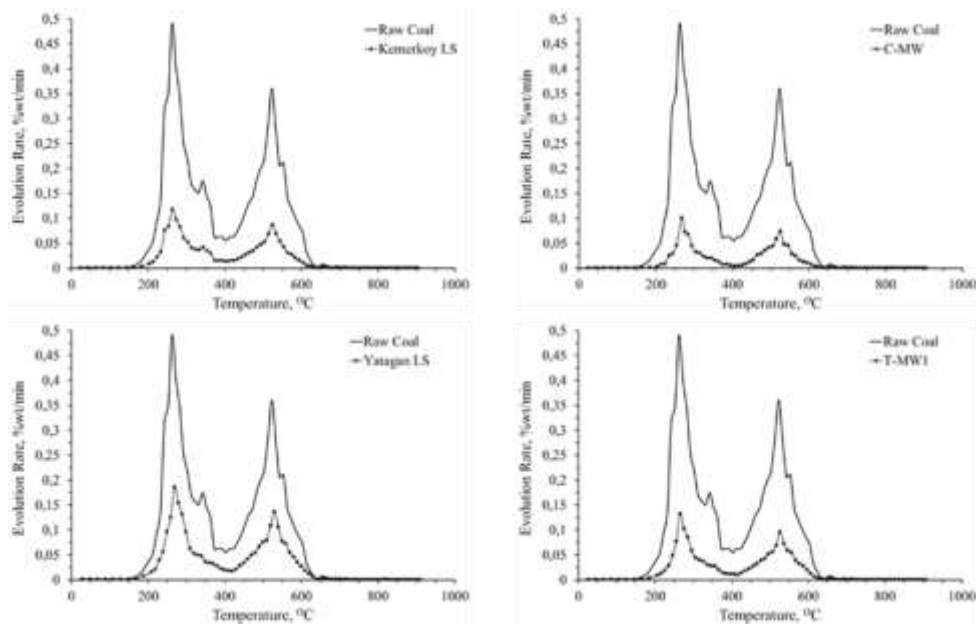

Fig. 5: SO_2 emission rates of ROM- and sorbent added coal samples.

SO₂ emission rates were also compared for ROM coal as well as Kemerköy and Yatağan limestone and C-MW and T-MW1 marbles waste added coal samples (Fig. 5). The highest reduction in the SO_2 emission rate was achieved with addition of C-MW marble waste and Kemerköy limestones. The decrease in SO_2 emission rates were also notable with the T-MW1 marble waste added coal and use of T-MW1 as a sorbent leads to a more effective SO_2 control than Yatağan limestone (Fig. 5). Use of Yatağan limestone reduces SO_2 emission rate, but at a lower extent in comparison with Kemerköy limestone and C-MW and T-MW1 marble wastes.

Possible correlations between SO_2 emission rates and $CaCO_3$ and $MgCO_3$ contents of the sorbents were examined (Fig. 6). A direct link between the $CaCO_3$ content of the sorbent and its SO_2 control capability is observed. C-MW marble waste and Kemerköy limestone are outstanding SO_2 sorbents and are also distinguished with high calcite contents. Despite the comparable $CaCO_3$ in T-MW1 to Kemerköy limestone and C-MW waste, SO_2 control with T-MW1 was slightly lower. This

was attributed to the comparatively higher $MgCO_3$ in T-MW1 (Table 1). With a decline in calcite content and/or increase in $MgCO_3$, higher SO_2 emission rates were seen (Fig.6).
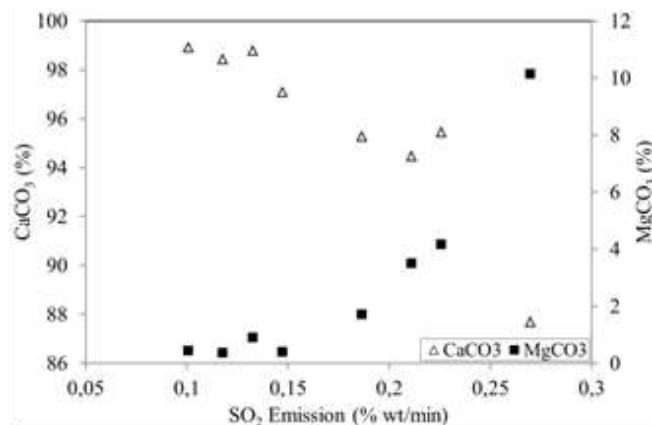

Fig. 6. SO_2 emission rates vs. $CaCO_3$ and $MgCO_3$ amounts in sorbents.

4. Conclusion

A comprehensive comparison of various marble wastes with limestones actively utilized as WFGD sorbents showed that wastes of some marble types may have comparable or even better physical and chemical features. Better liability to dissolution (reactivity) and more effective SO_2 control were achieved for marble waste types with high calcite and limited dolomitic contents. Higher grindability of some marbles waste types than limestones is another asset. Accordingly, a solid opportunity exists to use marble wastes as an alternative calcareous sorbent to limestones in WFGD systems. Yet, it might be perceptional to consider the wastes of all marble types appropriate as a SO_2 sorbent and a detailed assessment on the key sorbent characteristics is necessary to justify the compatibility of a given waste type for use in WFGD systems.

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