

Calcium sulfate as a possible oxidant in “green” silicon-based pyrotechnic time delay compositions

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Abstract: Chemical time delay detonators are used to control blasting operations in mines and quarries. Slow burning Si-BaSO₄ pyrotechnic delay compositions are employed for long time delays. However, soluble barium compounds may pose environmental and health risks. Hence inexpensive anhydrous calcium sulfate was investigated as an alternative “green” oxidant. EKV1 simulations indicated that stoichiometry corresponds to a composition that contains less than 30 wt. % Si. However combustion was only supported in the range of 30-70 wt. % Si. In this range the bomb calorimeter data and burn tests indicate that the reaction rate and energy output decrease with increasing silicon content. The measured burn rates in rigid aluminium elements ranged from 6.9 to 12.5 mm s⁻¹. The reaction product was a complex mixture that contained crystalline phases in addition to an amorphous calcium containing silicate phase. A reaction mechanism consistent with these observations is proposed.

Keywords: Silicon, Calcium sulfate, Time delay, Pyrotechnics

1 Introduction

Delay detonators are extensively employed in mining, quarrying and other blasting operations. They are used to facilitate sequential initiation of explosive charges in a pattern of boreholes [1]. The timing of the sequential initiation events is carefully chosen in order to control the fragmentation and throw of the rock being blasted. This approach also reduces ground vibration and air blast noise [1]. Both chemical and electronic time delay detonators are used to achieve the required time delays. The simplicity, ruggedness and low cost of pyrotechnic delays make them particularly attractive for high volume mining applications.

Numerous delay compositions, comprising mixtures of fuels and oxidizers, have been developed for different applications [1-2]. Some commercial pyrotechnic compositions contain heavy metal-based oxidizers, e.g. lead, barium and chromate compounds [3]. Such compounds are deemed environmentally unfriendly and pose a potential health hazard [3b]. This has led to the tightening of health and safety legislation and concerted efforts to find “green” replacements [3a, 4]. Silicon is a common fuel used in time delay time detonators [5]. Si-Pb₃O₄ and Si-BaSO₄ are currently commercially employed for short-time and long-time delays respectively. However, both lead and barium based oxidants have been earmarked for replacement, and alternative oxidants for use with silicon are sought. Hence the inexpensive compound anhydrous calcium sulfate was investigated as a potential alternative “green” oxidant.

2 Experimental

2.1 Materials

Ball milled Type 4 silicon was supplied by Millrox. The d₅₀ particle size was 2.1 μm (Mastersizer Hydrosizer

2000) and the specific surface area was 11 m²g⁻¹ (Micrometrics Tristar II BET, N₂ at 77 K). Anhydrous calcium sulfate was supplied by Industrial Analytical. It had a d₅₀ particle size of 3.8 μm (Mastersizer Hydrosizer 2000) and a specific surface area of 3.5 m²g⁻¹ (Micrometrics Tristar II BET, N₂ at 77 K). X-ray Diffraction (XRD) analysis of the silicon and calcium sulfate used in the experiments confirmed that both materials were of high purity. Figure 1 shows Scanning Electron Microscopy (SEM) pictures of the calcium sulfate and silicon used in this investigation.

2.2 Preparation methods

The silicon fuel content in the Si-CaSO₄ pyrotechnic composition was varied from 20 to 80 wt. %. The powders were mixed by brushing them several times through a 75 μm sieve. The compositions were pressed into 25 mm long aluminium tubes with an internal diameter of 3.6 mm and a wall thickness of 1.45 mm. The filling process started with two increments of a proprietary starter composition pressed with a 100 kg load. This was followed by repeated steps of adding two increments of the delay composition and pressing it with the same load until the tube was filled.

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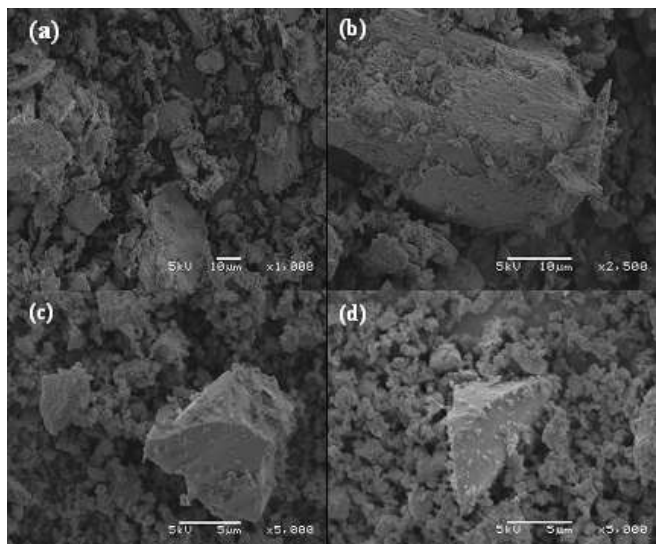


Figure 1. SEM pictures of (a) and (b) calcium sulfate; (c) and (d) silicon.

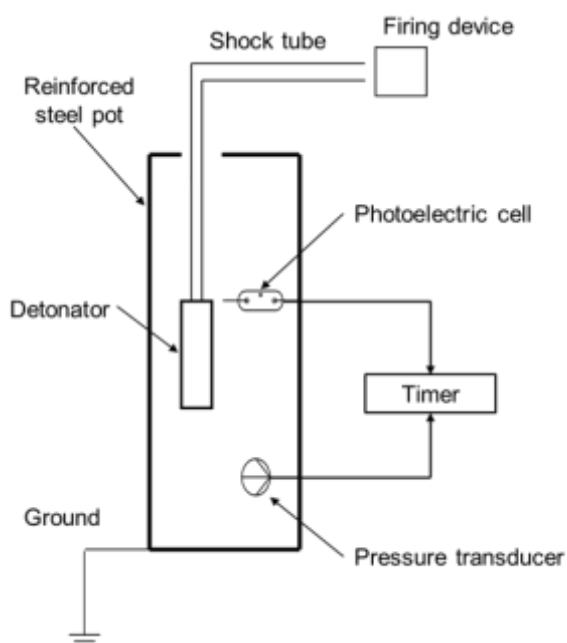


Figure 2. Firing and timing schematic used for burning rate measurements.

2.3 Burning rate measurements

The burning rates were determined using commercial detonator assemblies. The detonators comprised an initiating shock tube coupled to a rigid aluminium time delay element contained in an aluminium shell. This outer shell contained increments of lead azide primary explosive and pentaerythritol tetranitrate (PETN) as the secondary explosive. The way the actual delay time was determined is illustrated by the scheme in Figure 2. The shock tube was ignited by the firing device and the resultant flash was recorded by the photoelectric cell. This signal was sent to the timer as the initiating signal. After detonation, the pressure

transducer sent another signal to the timer which marked the end point of the timing sequence [6].

2.4 Characterization

Thermogravimetric Analysis (TGA) was performed on a Mettler Toledo A851 TGA/SDTA using the dynamic method. About 15 mg of powder sample was placed in an open 70 μL alumina pans. Temperature was scanned from 25 to 1300°C at a rate of 10°C min^{-1} with nitrogen flowing at a rate of 50 mL min^{-1} . Three runs were carried out for each sample.

Enthalpy measurements were carried out using a Parr 6200 calorimeter utilizing a 1104B 240 mL high strength bomb. Tap compacted test compositions (2 g) were initiated using 0.2 g of a proprietary starter. It was ignited with an electrically heated 30 gauge nichrome wire. The tests were carried out in a 3.0 MPa helium atmosphere. The variation of pressure with time was followed using a National Instruments piezoelectric transducer. A Parr Dynamic Pressure Recording System was used for data collection. The recording frequency was 5 kHz and 30000 data points were captured per test. Each composition was tested at least three times.

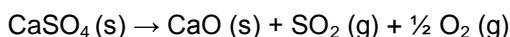
X-ray Diffraction (XRD) measurements were performed on a BRUKER D8 ADVANCE diffractometer with 2.2 kW $\text{CuK}\alpha$ radiation ($\lambda=1.54060 \text{ nm}$) fitted with a LynxEye detector with a 3.7° active area. Samples were scanned in reflection mode in the angular range 2° to 70° 2θ at a rate of 0.01° s^{-1} . The generator settings were 40 kV and 40 mA. Data processing and analysis were carried out using the BRUKER DIFFRAC^{Plus} - EVA evaluation program. Quantitative XRD analyses were performed according to the Rietveld method using DIFFRAC^{Plus} TOPAS software. The powdered residues were spiked with known proportions of corundum, a highly crystalline material. This made it possible to determine the amorphous content from the recorded diffractograms using the Rietveld method as discussed by Ward and French [7].

Single point sulfur analyses were performed on an Eltra CS 800 double dual range carbon-sulfur analyzer. Samples of the reaction products weighing ca. 0.2 g were milled and sieved to <75 μm . The samples were homogenized by slow rotation in a ceramic crucible with iron and tungsten chips. The instrument was calibrated using the Euronorm-CRM 484-1 Whiteheart malleable iron, Euronorm-CRM 058-2 sulfur steel and Euronorm-CRM 086-1 carbon steel standards. The instrument stability was monitored using the Council for Geoscience laboratory in-house soil reference standards. The sulfur detection limit was 0.009 wt. %.

3 Results

3.1 Thermal stability of reactants

Figure 3 shows the thermal stability of the silicon and calcium sulfate in a nitrogen atmosphere. The silicon showed no significant change in mass between 25°C and 600°C. However, a mass increase associated with the formation of silicon nitride was noted above 600°C. The anhydrous CaSO₄ was stable beyond 1000°C with the onset of decomposition above 1100°C. Previous TGA results indicate that the onset temperature for the decomposition falls in the range of 1080 °C to 1300°C [8]. Depending on the partial pressures of SO₃, SO₂ and O₂, the thermal decomposition of CaSO₄ takes place according to either Scheme 1 or Scheme 2 [9]. Complete decomposition to CaO results in a theoretical mass loss of 59%.



Scheme 1. Thermal decomposition of anhydrous calcium sulfate resulting in CaO (s) with a combination of SO₂ and O₂ as gaseous products.



Scheme 2. Thermal decomposition of anhydrous calcium sulfate resulting in CaO (s) with SO₃ as the only gaseous product

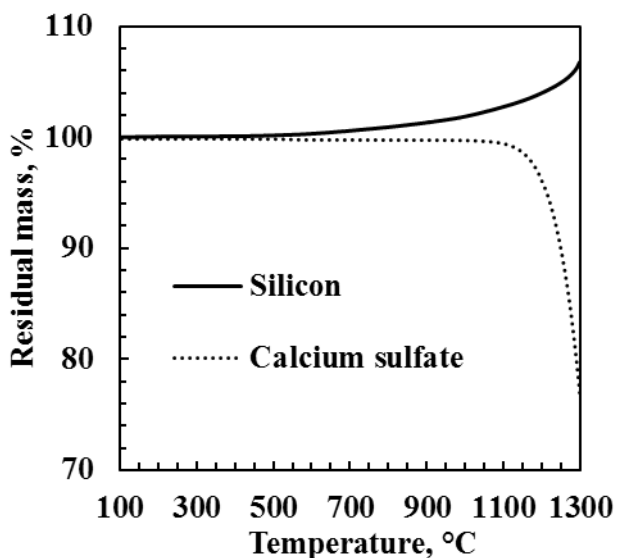


Figure 3. TGA results for silicon and calcium sulfate recorded in a nitrogen atmosphere.

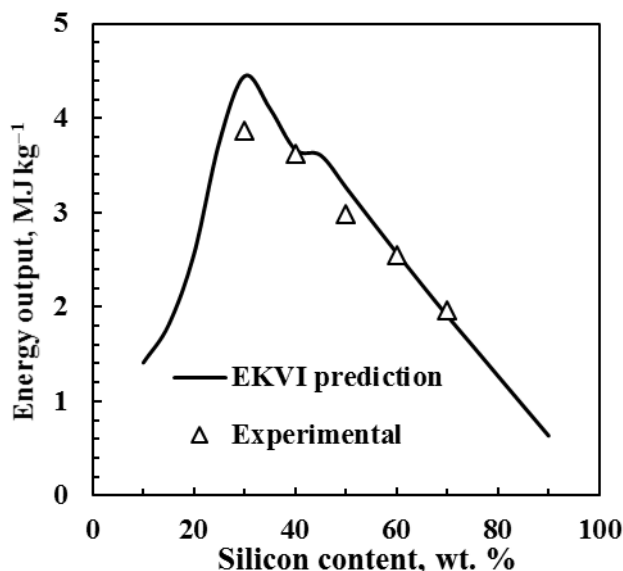


Figure 4. Comparison of experimental energy outputs obtained with the bomb calorimeter in a helium atmosphere with EKVI simulations for Si-CaSO₄.

3.2 Experimental and theoretical energy output measurements

The effect of the fuel content on the energy output of the Si-CaSO₄ formulations is shown in Figure 4. Ignition and propagation was only sustained in the range of 30 to 70 wt. % silicon. Compositions containing 20 or 80 wt. % silicon failed to propagate. The energy output decreases approximately linearly with increasing silicon content. The outputs ranged from 3.87 to 1.97 MJ kg⁻¹. The 30 wt. % silicon composition, which is the closest to stoichiometry, had the highest energy output [10]. Thermochemical predictions made using the EKVI thermodynamic software package over the range 10 to 90 wt. % silicon are also shown in Figure 4. The calculated exothermicity values from the EKVI program agreed reasonably well with the measured values. This suggests that the metal-oxidant reaction proceeded via the thermodynamically favoured pathway. Table 2 shows the constant-volume adiabatic reaction temperatures calculated with the EKVI code. There is a clear dependency of the adiabatic temperature on stoichiometry with the 30 wt. % silicon composition predicted to have the highest reaction temperature of 1685°C.

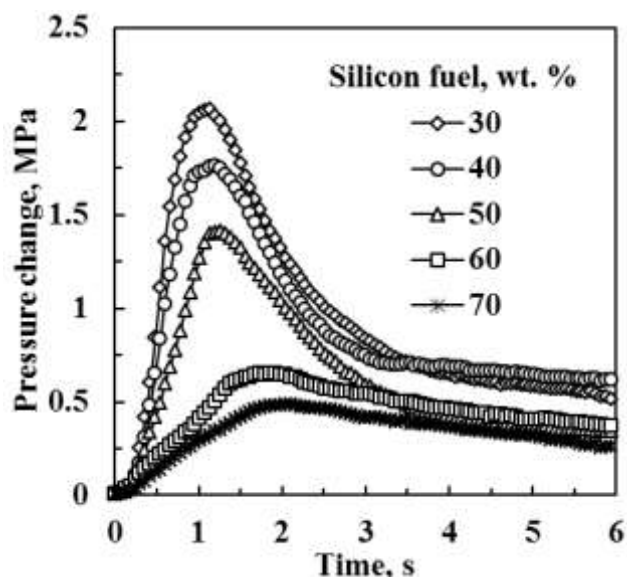


Figure 5. Pressure increase with time for different Si-CaSO₄ compositions during the bomb calorimetry experiments in a helium atmosphere.

Table 1. Energy output and peak pressures, times to reach the peak pressure and the maximum pressurization rates extracted from the relative pressure-time profiles measured in the bomb calorimeter

Si content (wt. %)	30	40	50	60	70
Energy output (MJ kg ⁻¹)	3.87	3.62	2.98	2.55	1.97
P_{max} (MPa)	2.06	1.76	1.41	0.65	0.49
t_{max} (s)	1.20	1.28	1.28	1.84	2.08
dP/dt_{max} (MPa s ⁻¹)	4.45	3.08	1.82	0.60	0.40

Table 2. Calculated maximum pressure differences assuming that all the CaSO₄ in the samples placed in the bomb calorimeter decomposed according to either Scheme 1 or 2, and adiabatic reaction temperatures predicted with the EKV1 thermochemistry simulations

Si content (wt. %)	30	40	50	60	70
Scheme I (MPa)	0.16	0.14	0.11	0.09	0.07
Scheme II (MPa)	0.11	0.09	0.08	0.06	0.05
Adiabatic reaction temperature (°C)	1684	1429	1300	1058	810

3.3 Pressure – time analysis

Time-dependent changes in pressure, relative to the initially applied helium pressure of 3.0 MPa, are shown in Figure 5. A summary of the information extracted from the pressure-time relationships is presented in Table 1. There are clear trends with the rate of pressure rise as well as the maximum peak pressure decreasing with increasing silicon content. This correlates with the observation of decreasing energy

with increasing silicon content in this composition range. There was a noticeable time delay before the pressure rose. This time lag was almost independent of the fuel content of the composition. Figure 5 reveals higher residual pressure differences at the end of the six second pressure test for the 30 and 40 wt. % silicon formulations compared to the other three compositions. This could either be due to a higher residual temperature caused by the higher energy outputs or to the generation of more gas. The residual pressure differences, after cooling to room temperature, were calculated assuming that the entire calcium sulfate present in the test sample decomposed completely according to either Scheme 1 or 2 (Table 2). Maximum pressure differences of 0.16 and 0.11 MPa, respectively, were found for the 30 wt. % composition. The theoretical results are considerably lower than all the experimentally measured residual pressures after six seconds. This suggests that the higher differential pressures were caused by residual heating effects.

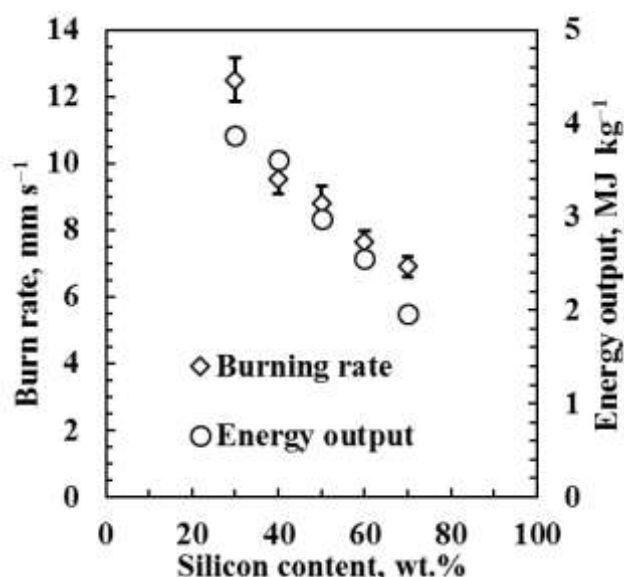


Figure 6. The effect of fuel content on the burning rate and energy output of Si-CaSO₄ compositions.

3.4 Burning Rates

Figure 6 shows the effect of stoichiometry on the burn rate of the Si-CaSO₄ system. The burn rate decreased with increasing silicon content. The composition containing 30 wt. % Si burned fastest (12.5 mm s⁻¹) whilst the 70 wt. % Si composition was the slowest (6.9 mm s⁻¹). This burning rate is similar to the burning rate of Si-BaSO₄ compositions (4 – 9 mm s⁻¹) [11] but is much slower than the range reported for Si-Pb₃O₄ compositions (40 – 257 mm s⁻¹) [12].

Figure 6 also shows that the burning rate and the energy output decrease in tandem as the fuel content increases. According to Khaikin and Merzhanov [13] the burning rate varies inversely with

the square root of the energy output. However, according to Hill *et al.* [14], the burning rate should be directly proportional to the energy output and this is roughly the case for the present data.

3.5 XRD analysis of reaction products

Quantitative X-Ray diffraction (XRD) analysis was performed on the reaction products. See Table 3. This information was used to deduce a reaction mechanism and to establish whether the combustion products were environmentally benign. The major crystalline products detected were calcium sulfide (CaS), pseudowollastonite ($\text{Ca}_3(\text{SiO}_3)_3$), quartz (SiO_2) and unreacted silicon. Trace amounts of bismuth metal and bismuthinite (Bi_2S_3) were also detected. These impurities derived from the proprietary bismuth oxide based starter that was used to ignite the various formulations. These results also revealed the presence of a significant amount of an amorphous phase in the reaction products. No unreacted calcium sulfate was detected. This was expected since gypsum thermally degrades below the high pyrotechnic reaction temperatures.

Table 3 also reports the sulfur analysis of the solid reaction residues. Sulfur was essentially retained the form of calcium sulfide with minute amounts present in the amorphous phase. A sulfur mass balance enabled the determination of the amount of gas produced during the reaction assuming no impurities in the reactants and that SO_2 is the only gas evolved. Depending on the stoichiometry, the gas evolved at standard temperature and pressure conditions, ranged from 29.2 to 57.5 $\text{cm}^3 \text{g}^{-1}$. This is considerably higher than the 10 $\text{cm}^3 \text{g}^{-1}$ generally taken as the upper limit for classification as a gasless composition [15].

Mass balances on the other elements were also carried out. In particular, the Si:Ca ratio in the amorphous phase exceeded three for all the compositions. This indicates that the amorphous phase was predominantly composed of silica (SiO_2).

Table 3. Quantitative analysis of the reaction products identified from the Si- CaSO_4 pyrotechnic composition using XRD as well as an analysis of the total sulfur content in the solid products

Phase	Formula	30	40	50	60	70
Silicon	Si	2.7	17.7	26.8	36.3	41.1
Quartz	SiO_2	2.6	4.0	4.9	1.1	1.2
Pseudowollastonite	$\text{Ca}_3(\text{SiO}_3)_3$	19.2	25.5	13.6	9.8	10.4
Calcium sulfide	CaS	9.2	14.4	13.6	10.7	1.9
Bismuth	Bi	0.6	2.4	1.3	1.5	1.7
Bismuthinite	Bi_2S_3	1.2	1.9	1.3	1.1	0.7
Amorphous ^a		64.5	34.1	38.5	39.5	43.1
Si/Ca ratios						
Reagents		2.08	3.23	4.84	7.27	11.3
Crystalline phase		1.04	2.19	3.77	5.99	13.6
Amorphous phase		3.02	6.64	7.47	10.2	9.15
Sulfur analysis	wt. %	9.9	5.5	5.3	4.0	3.1
Gas evolved	$\text{cm}^3 \text{g}^{-1}$	51.2	63.5	48.0	39.8	28.8

^aMainly silica

Table 4. Major reaction products of the Si- CaSO_4 composition predicted using EKVI thermodynamics code under adiabatic conditions

Formula	10	20	30	40	50	60	70	80	90
SO_2 (g)	0.5	10.6	-	-	-	-	-	-	-
S_2 (g)	3.7	12.7	-	-	-	-	-	-	-
SiS(g)	-	-	3.7	0.3	-	-	-	-	-
Si (s)	-	-	0.1	15.2	29.4	43.5	57.6	71.8	85.9
SiO_2 (s)	12.2	19.5	57.5	52.6	44.1	35.3	26.5	17.7	8.8
CaS (s)	-	-	32.9	31.5	26.5	21.2	15.9	10.6	5.3
$\text{Ca}_3\text{Si}_2\text{O}_7$ (s)	24.3	57.2	5.9	0.5	0.1	-	-	-	-
CaSO_4 (s)	59.4	-	-	-	-	-	-	-	-
Total	100	100	100	100	100	100	100	100	100

Table 4, Figure 7 and Figure 8 provide details of the EKVI simulation results for the Si- CaSO_4 formulation. A comparison of the data reveals that the experimental silicon conversions were similar for the 30 - 50 wt. % Si compositions. However, the remaining compositions showed higher conversions than the predictions of the EKVI thermochemistry simulations (Figure 9).

The reaction product spectra predicted with the EKVI were similar to those found experimentally. However, according to the EKVI simulation, all the test compositions essentially qualify as "gasless" since the predicted amount of gas produced was minimal. Exceptions were seen in the case of the low silicon content formulations i.e. 10 and 20 wt. % Si, where quantifiable amounts of SO_2 (g) and elemental S_2 (g) were predicted. In the case of 30 wt. % silicon composition SiS gas formation was predicted. The major solid phases predicted were SiO_2 , CaS, $\text{Ca}_3\text{Si}_2\text{O}_7$ and unreacted silicon. The programme predicted complete conversion of the CaSO_4 to CaS. However, $\text{Ca}_3\text{Si}_2\text{O}_7$ was only prominent in the 10 and 20 Si wt. % compositions. It should be noted that the EKVI database includes wollastonite CaSiO_3 but does not contain pseudowollastonite. Obviously this influenced the predictions made with the software.

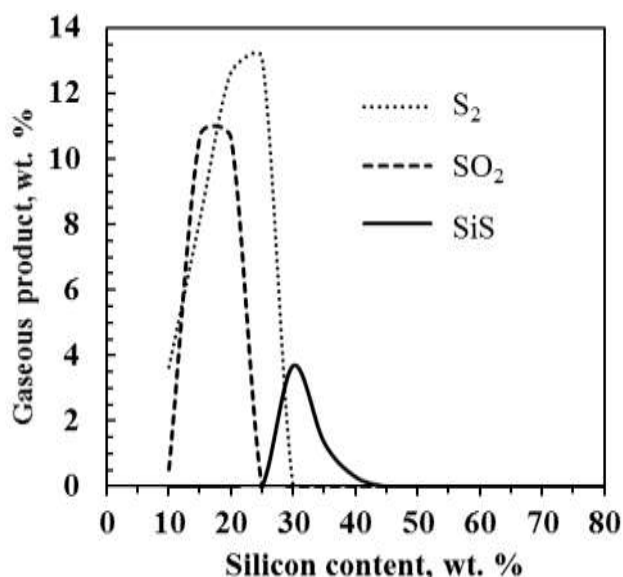


Figure 7. Gaseous products released during the combustion of the Si-CaSO₄ pyrotechnic composition predicted with the EKVI thermodynamics software.

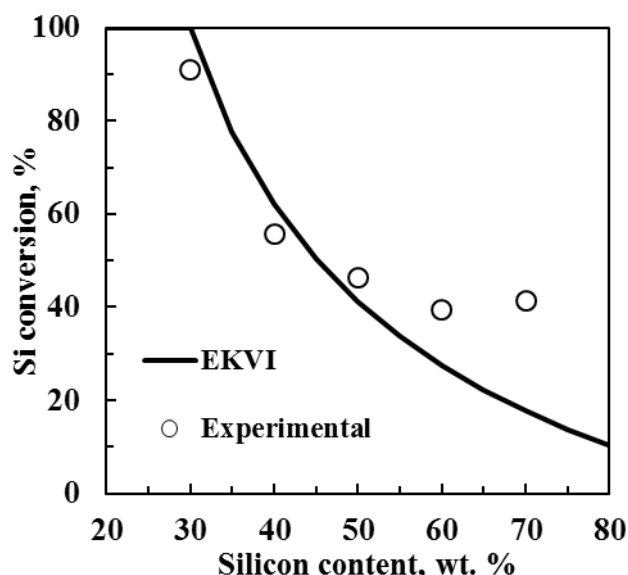


Figure 9. Comparison of the conversion of silicon based on XRD reaction products and the reaction products predicted using the EKVI thermodynamics software.

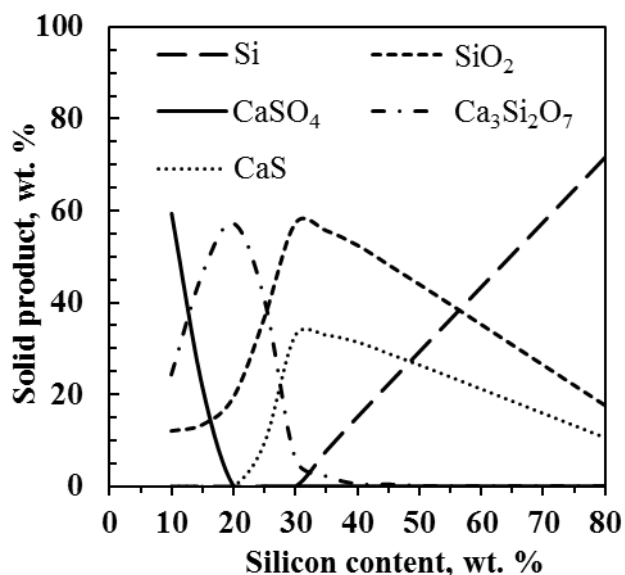
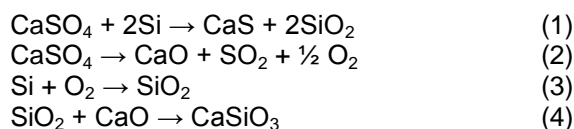


Figure 8. Solid products obtained during the combustion of the Si-CaSO₄ pyrotechnic composition predicted with the EKVI thermodynamics software.

4 Discussion

Pseudowollastonite and calcium sulphide were the dominant crystalline phases in the residue left by the Si-CaSO₄ reaction. The former is a high temperature polymorph of wollastonite (CaSiO₃). Gladun and Bashaeva [16] performed a thermodynamic analysis of possible reactions for high temperature synthesis of wollastonite. They found that it can be obtained in the temperature range 1000 to 1400°C. Their results, the presented XRD and TGA data as well as the findings of Mu and Zaremba [17] can be explained by the set of reactions proposed in Scheme 3:



Scheme 3. Proposed reactions steps taking place in the reaction of the Si-CaSO₄ pyrotechnic composition.

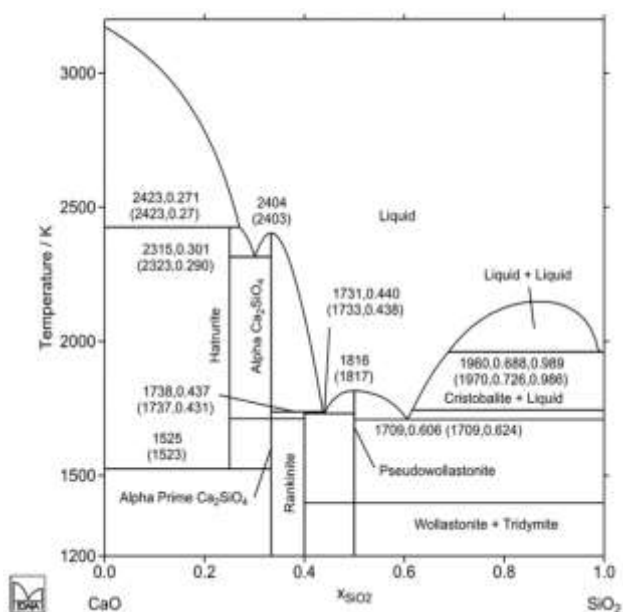


Figure 10. Phase diagram for the system CaO-SiO₂ reproduced with permission from the authors of [18].

Figure 10 shows a CaO-SiO₂ phase diagram calculated using the MTDATA software developed by Davies, *et al.* [18]. The phase diagram shows that several compounds or compound combinations are formed at different temperatures and CaO-SiO₂ ratios. A mass balance, which was carried out to establish the Si:Ca ratio, revealed that the amorphous phase is predominantly made up of SiO₂. Table 3 shows that the silicon to calcium ratio in the amorphous phase of all the residues was much higher than the 1:1 ratio expected for wollastonite, varying from 3.02 to 10.2. These correspond to SiO₂ mol fractions of 0.75 to 0.91 in Figure 10. This means that the formation of the pseudowollastonite and the amorphous phase identified and quantified by XRD analysis can be attributed to a combination of reactions 3 and 4 of Scheme 4. It also implies that these phases were most likely fixed in the square temperature-composition region second from below and on the far right hand side of the phase diagram in Figure 10. It is worth noting that the reported solid product analysis only provides an idea of the actual reaction products since the analysis was performed at room temperature while the theoretical adiabatic temperature can reach 1684°C. Furthermore, the cooling rate experienced by the residue may have influenced the distribution between crystalline and the amorphous phases.

4 Conclusion

Calcium sulfate was shown to be a viable oxidant for silicon in slow-burning time delay compositions. The energy outputs, pressure-time profiles and burning rate measurements all showed a general trend of decreasing with increasing silicon content. XRD analysis of the reaction products revealed that the products were a composite mixture of crystalline and amorphous phases. The fair agreement between the

EKVI simulation results and the present experimental data suggests that the reaction proceeds by the thermodynamically favoured pathway. Both the reactants and the products of the composition tested are environmentally benign.

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