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**Achieving superior ignition and combustion performance of Al/I<sub>2</sub>O<sub>5</sub>  
biocidal nanoenergetic materials by CuO addition**

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**Abstract:** It was found that all iodine-containing biocidal energetic materials has a relatively long ignition delay upon combustion. A shorter ignition time (from the thermal trigger to the peak pressure) for Al/iodine oxides might further boost their combustion performance due to their high reactivity and high gas release rate. To achieve this goal, a secondary oxidizer, CuO, is incorporated into Al/I<sub>2</sub>O<sub>5</sub> at different mass content keeping the overall thermite stoichiometry constant. The ternary Al/I<sub>2</sub>O<sub>5</sub>/CuO thermites were characterized in ignition using a T-jump ignition temperature set up, and in combustion in a constant volume combustion cell. Consequently, all ternary thermites outperform traditional Al/I<sub>2</sub>O<sub>5</sub> counterpart with an optimum for 80/20 wt% of I<sub>2</sub>O<sub>5</sub>/CuO. This later composition ignites in 0.01 ms (30 times shorter than Al/I<sub>2</sub>O<sub>5</sub>) and produces peak pressure and pressurization rate of ~4 and 26 times greater than those produced by Al/I<sub>2</sub>O<sub>5</sub>. A series of additional characterizations using Fourier-transform infrared spectroscopy, Differential Scanning Calorimetry, Electrical/Thermal conductivity measurement, etc., permitted to unravel the cause of such improvement and to propose a reaction mechanism for this ternary Al/I<sub>2</sub>O<sub>5</sub>/CuO system. From an applications point of view, this study proposes a facile, inexpensive and efficient way to enhance the combustion performance of Al/I<sub>2</sub>O<sub>5</sub> biocidal nanoenergetic materials.

**Novelty and significance statement:** we incorporated a secondary oxidizer CuO into Al/I<sub>2</sub>O<sub>5</sub> system with the goal to shorten its ignition delay without penalizing their combustion performance (pressure development). Surprisingly the CuO addition not only eliminated the ignition delay of Al/I<sub>2</sub>O<sub>5</sub> in a constant-volume combustion cell but also demonstrated significant enhancement on peak pressures, pressurization rates, flame temperatures and

shorter ignition delay compared to that of either Al/CuO or Al/I<sub>2</sub>O<sub>5</sub>. Multiple characterization tools were used to identify the cause of such improvement. Then we verified that CuO has a much better thermal conductivity than I<sub>2</sub>O<sub>5</sub>, which improves the thermal transfer within the Al/I<sub>2</sub>O<sub>5</sub>/CuO thermites and thus creates a positive effect on its combustion. This work not only proposed a new high performing biocidal energetic material containing 80/20 wt% of I<sub>2</sub>O<sub>5</sub>/CuO but also unravel the reasons of enhancement on ignition and combustion performance.

**Authors Contributions:** T.W. conceived the idea, designed and carried out the present work. T.W., M.R.Z., and C.R. wrote the paper. E.H. and D.J.K. carried out calculations on constant-volume thermite combustion. H.W. and D.J.K. assisted T.W. in combustion cell test and flame temperature measurement. M.R.Z. and C.R. supervised this research.

**Keywords:** Biocidal nanoenergetic materials, iodine oxide, copper oxide, combustion, reactivity, synergetic effect.

## 1. Introduction

Anti-biological warfare agents with high-efficiency neutralization have gained increased attention due to an increasing threat of bioterrorism [1–5]. The current thinking is that an ideal neutralization process should generate not only a high temperature, but also release a long-lasting biocidal agent [6–9]. This is because a conventional energetic materials can result in low neutralization efficiency since they rely solely on a thermal neutralization pulse which is spatially distributed, may not provide enough thermal energy for long enough to kill the spores [10]. Therefore, it has been proposed that simultaneously delivering a rapid thermal pulse with a remnant biocidal agent would prolong the exposure time and improve the

inactivation process [11]. Iodine-containing energetic materials have shown the most promise because of their excellent biocidal properties [12] compared to other biological energetic materials [13–15]. Different methods have been reported for incorporating elemental iodine into energetic materials [12,16–18]. Dreizin et al. employed mechanically-alloyed aluminum-iodine composites as a fuel in energetic formulations and the initiation and combustion tests in air indicated that higher iodine concentration lowers initiation temperatures without substantially impacting the combustion temperatures [8]. They also found improvements in regards to pressurization rate and maximum pressure at constant volume with 15 wt.% and 20 wt.% of I<sub>2</sub>. Wang et. al physically added iodine molecules into Al/CuO thermite and Al/PVDF systems, and found that the reaction rate was significantly decreased with increasing iodine content while a burn rate comparable to that of Al/PVDF film could be achieved with high iodine content (67 wt.%) when incorporated into a laminated structure [17,19].

Another efficient approach is to use iodine-containing oxy-compounds as an oxidizer - particularly iodine oxides and/or iodic acids. Among all the iodine oxides/iodic acids (I<sub>2</sub>O<sub>5</sub>, I<sub>4</sub>O<sub>9</sub>, HI<sub>3</sub>O<sub>8</sub>, HIO<sub>3</sub>, H<sub>5</sub>IO<sub>6</sub>, etc [20–22]), I<sub>2</sub>O<sub>5</sub> is the most studied oxidizer in thermite systems [10,23–26] due to its relatively high iodine content (~76% iodine mass fraction) and high oxidizing power. In these studies, aluminum nanoparticles (nano-Al) with different sizes were chosen as the fuel due to its high reaction enthalpy, thermal conductivity and availability. With reported propagation velocities of up to ~2,000 m.s<sup>-1</sup> for loose ball-milled nano-aluminum and nano-scaled I<sub>2</sub>O<sub>5</sub> (~10 nm) [26], I<sub>2</sub>O<sub>5</sub> shows a high potential in aluminum-based thermites as an extremely aggressive oxidizer. Constant volume combustion tests also show nano-Al/micro-I<sub>2</sub>O<sub>5</sub> outperforms traditional aluminum-based thermites such as Al/micro-CuO and Al/micro-Fe<sub>2</sub>O<sub>3</sub>. [10] A pre-ignition reaction is thought to trigger ignition in which ionic I<sub>2</sub>O<sub>5</sub> fragments diffuse into the alumina-passivated shell, and create

exothermic reactive complexes [25,27]. However, this mechanism is far from clear as Smith et al. reported that such pre-ignition reaction was not found for Al/nano crystalline  $I_2O_5$ . [28] Wu et al. reported that aerosol-route synthesized iodine oxides/iodic acids outperform the corresponding commercial materials in combustion cell tests, where in particular Al/(aerosol-route synthesized)  $a-HI_3O_8$  has the highest pressurization rate, highest peak pressure, and shortest burn time among all iodine-containing composites [29]. Later, Wu et al. employed carbon as an additive or main fuel into iodine oxides-based energetic materials and reported that carbon addition can lower initiation and iodine release temperatures due to a surface interaction between carbon and iodine oxide [30]. Aluminum combined with iodine oxides/iodic acids shows long ignition delay ( $\sim 0.3$  ms) [29].

In this work, with the aim to increase the reactivity, i.e. shorten the ignition delay of 0.3 ms observed for all iodine oxides-based energetic, a strong oxidizer such as CuO [31–33] is added into the Al/ $I_2O_5$  thermites at different mass ratio.  $I_2O_5$  is chosen because it is relatively easy to prepare in comparison to other iodine oxides via aerosol spray pyrolysis [16,29], and is physically mixed with Al nanopowders. Ignition and combustion of the as-prepared ternary Al/ $I_2O_5$ /CuO thermites are characterized to determine the ignition delay, flame temperatures, pressure development in a constant-volume combustion cell. We find that the addition of CuO into Al/ $I_2O_5$  thermites leads to a new promising biocidal nanoenergetic materials featuring reduced ignition delays ( $\div 30$ ), shorter burn times ( $\div 2$ ), higher combustion temperatures ( $\sim 4650$  °C against  $\sim 3900$  °C). Further, additional experiments and analyses including thermal analysis permitted to conclude on a double positive effect of CuO on the Al/ $I_2O_5$  thermite. Not only the CuO is a strong oxidizer with limited influence on the low temperature decomposition of  $I_2O_5$  but also, CuO features a much higher thermal conductivity than  $I_2O_5$ , which could favor the thermal transport governing the reaction

process. We also experimentally demonstrated that 20 wt% of CuO leads to the best ignition and combustion properties.

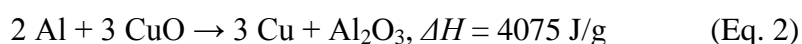
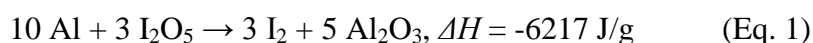
## 2. Experimental

### 2.1 Materials

The aluminum nanopowders (Al) (Alex, ~80 nm) were purchased from Novacentrix. The active Al was 81% by mass, determined by thermogravimetric analysis. Iodic acid and nanosized CuO (~100 nm) purchased from Sigma-Aldrich were directly used as received. All the other chemicals were of analytical grade and used as purchased without further treatment. I<sub>2</sub>O<sub>5</sub> was prepared via aerosol spray pyrolysis with a silica gel regeneration temperature of 80 °C and a furnace temperature of 340 °C that is slightly different from the preparation method for a-I<sub>2</sub>O<sub>5</sub> in our previous work [29].

### 2.2 Preparation of ternary thermites

Aluminum was stoichiometrically mixed with I<sub>2</sub>O<sub>5</sub> and/or CuO based on the following equation in hexane followed by 30 minutes of sonication.



The detailed chemical constituents of thermites tested is summarized below in **Table 1**. After room temperature evaporation of the solvent in a desiccator, the solid thermite powders were used. The percentages in Al/I<sub>2</sub>O<sub>5</sub>/CuO\_x% are referring to the molar percentage of aluminum that would be consumed by CuO (the far-right column in **Table 1**). Take sample Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20% for example, 20% of the aluminum would stoichiometrically react with CuO and the remaining 80% of aluminum would react with I<sub>2</sub>O<sub>5</sub>. To simplify the following discussion regarding the ignition and combustion properties of different Al/I<sub>2</sub>O<sub>5</sub>/CuO\_x% samples, we will refer to x% simply as CuO loading.

**Table 1.** Chemical constituents of various thermites powders tested in this work <sup>a</sup>.

Thermites	Weight, mg				Weight percentage of CuO in oxidizers	Molar percentage of Al reacting with CuO
	Al	I <sub>2</sub> O <sub>5</sub>	CuO	Total		
Al/I <sub>2</sub> O <sub>5</sub>	6.3	18.7	—	25.0	0%	0%
Al/I <sub>2</sub> O <sub>5</sub> /CuO_20%	6.1	15.1	3.8		20%	20%
Al/I <sub>2</sub> O <sub>5</sub> /CuO_40%	5.9	11.1	8.0		42%	40%
Al/I <sub>2</sub> O <sub>5</sub> /CuO_60%	5.7	6.2	13.1		68%	60%
Al/I <sub>2</sub> O <sub>5</sub> /CuO_80%	5.6	3.5	15.9		80%	80%
Al/CuO	5.5	—	19.5		100%	100%

<sup>a</sup>: Al active content is 81%; all thermites are prepared in the stoichiometric condition.

### 2.3. Chemical and thermal characterizations

Attenuated total reflection (ATR) FTIR spectra of the thermite powders were collected using a Nicolet iS-50R spectrometer equipped with a room temperature deuterated triglycine sulfate (DTGS) detector FTIR spectroscopy. A Thermo Scientific Smart iTX accessory was installed to collect the ATR spectra shown here at 4 cm<sup>-1</sup> resolution and averaged over 30 scans. The thermal decomposition of the thermite powders was characterized under a ramping heating profile at 10°C/min by a METTLER TOLEDO TGA 2 and a NETZSCH DSC 404 F3 Pegasus device equipped with a DSC-Cp sensor type S over a temperature ranging from ambient to 1000 °C. Experiments were performed with ~5 mg of composites in platinum crucibles in (99.998% pure) at a flow rate of 20 mL/min. The traces are normalized by the mass of energetic composite material.

### 2.4. Combustion tests

Combustion properties of themites were evaluated in a constant-volume combustion cell, with simultaneous pressure and optical emission measurements. 25 mg of thermite powders



was loosely loaded inside the cell (constant volume,  $\sim 20 \text{ cm}^3$ ) and ignited by a resistively heated nichrome wire. The wire touches the top of the thermite powder and the reaction propagate downward upon ignition. The temporal pressure and optical emission from the thermite reaction were measured using a piezoelectric pressure sensor and a photodetector, respectively. By plotting the data as shown in **Figure S1**, pressurization rate, maximum pressure and burn time can be obtained and used for evaluation of the combustion performance. Pressurization rate is calculated by dividing the first peak pressure by the corresponding time. Burn time is defined as the full width of the half maximum of the optical profile. More detailed information on the combustion cell test can be found in our previous publications [29,34].

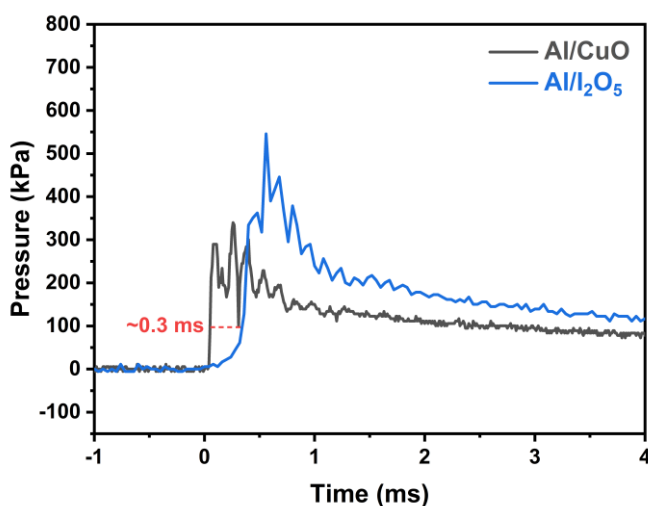
## **2.5. Ignition tests**

The ignition of the thermite was investigated using a T-Jump/TOFMS as in several previous papers [35,36]. In brief, a  $\sim 1 \text{ cm}$  long platinum wire ( $76 \mu\text{m}$  in width) with a thin layer coating of oxidizer sample was rapidly joule-heated to about  $1200 \text{ }^\circ\text{C}$  by a  $3 \text{ ms}$  pulse at a heating rate of  $\sim 5 \times 10^5 \text{ }^\circ\text{C}\cdot\text{s}^{-1}$ . A high-speed camera (Vision Research Phantom v12.0) was also employed to identify the point of initiation and burn time. The current and voltage signals were recorded, and the temporal temperature of the wire was measured according to the Callendar–Van Dusen equation [30,36]. Mass spectra were measured every  $0.1 \text{ ms}$ . Ignition delay of thermite reactions in T-jump experiments were defined and measured as the time of ignition where the first light is observed from high speed imaging of the whole combustion event. Then, applying the ignition delay in the temporal temperature curve of the wire, ignition temperatures of thermite reactions were measured. Each measurement was repeated at least 3 times.

## **3. Results and discussion**

### **3.1. Ternary Al/I<sub>2</sub>O<sub>5</sub>/CuO thermites outperforming Al/I<sub>2</sub>O<sub>5</sub>**

**Figure 1** plots the temporal pressure profiles of Al/CuO and Al/I<sub>2</sub>O<sub>5</sub>, I<sub>2</sub>O<sub>5</sub> being synthesized by aerosol-route [29] characterized in a constant volume combustion cell. We clearly see the ~0.3 ms ignition delay between the two pressure history profiles of the two thermites systems, as mentioned in the introduction. Since aerosol-route synthesized I<sub>2</sub>O<sub>5</sub> have particles sizes of ~0.5 μm (span from 0.1 to 1 μm), the ignition delay might be caused by the difference between the particle sizes of these two oxidizers [29]. However, the smallest size of I<sub>2</sub>O<sub>5</sub> achievable remains larger than 0.5 μm [16,37] leaving a low possibility of testing nanosized I<sub>2</sub>O<sub>5</sub> (< 100 nm).

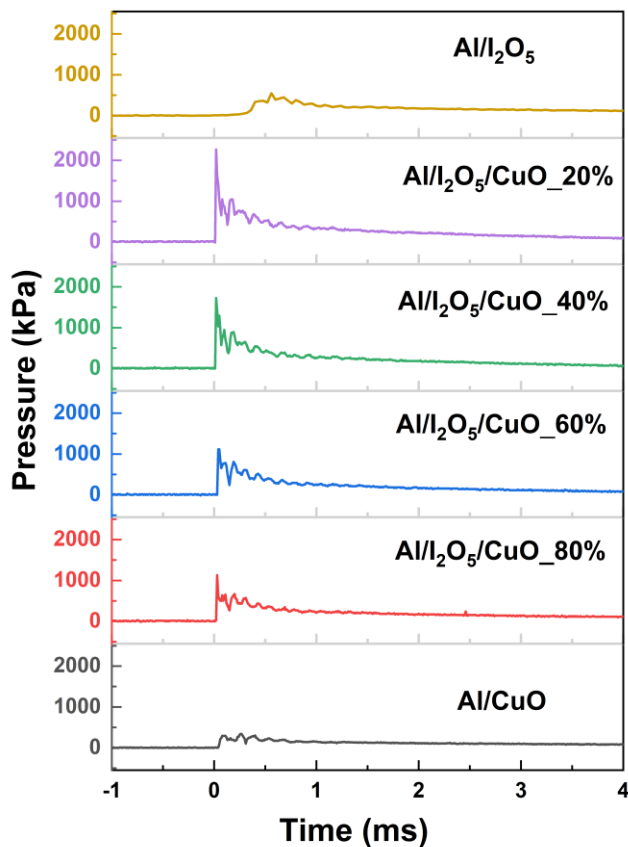


**Figure 1.** Temporal pressure traces of Al/CuO and Al/I<sub>2</sub>O<sub>5</sub>.

This is the reason why we propose to incorporate nanosized CuO into the Al/I<sub>2</sub>O<sub>5</sub> thermite powders varying the ratio between the two oxidizers while maintaining the same stoichiometric condition. They are referred as Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20%, Al/I<sub>2</sub>O<sub>5</sub>/CuO\_40%, Al/I<sub>2</sub>O<sub>5</sub>/CuO\_60% and Al/I<sub>2</sub>O<sub>5</sub>/CuO\_80% (see **Table 1** for more details). **Figure 2** presents their temporal pressure profiles obtained in the pressure cell and compared with Al/CuO and Al/I<sub>2</sub>O<sub>5</sub> obtained in the same conditions to serve as reference. As expected, upon addition of CuO, the ignition delay disappeared. And, surprisingly, all four ternary systems significantly outperform the Al/I<sub>2</sub>O<sub>5</sub> and Al/CuO in terms of the peak pressure whereas Al/CuO features smaller gas production (5.4 mmol.g<sup>-1</sup>) in comparison with Al/I<sub>2</sub>O<sub>5</sub> (6.3 mmol.g<sup>-1</sup>) [38]. One

would expect to obtain weakened combustion performance from the ternary systems when CuO is added to Al/I<sub>2</sub>O<sub>5</sub>.

A summary of the pressure development results is more easily digested in **Figure 3a-b** confirming that addition of CuO increases the peak pressure and pressurization rate of Al/I<sub>2</sub>O<sub>5</sub> even at small mass loadings of CuO. Evidently, Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20%, gives the best performances: the ignition delay is reduced by almost 30 times as opposed to Al/I<sub>2</sub>O<sub>5</sub> and pressure peak is increased by roughly 4 and 26 times, compared to Al/I<sub>2</sub>O<sub>5</sub> and Al/CuO, respectively. With higher CuO loading, the improvement is not as important but is still better than the neat formulation of either oxidizer with Al.

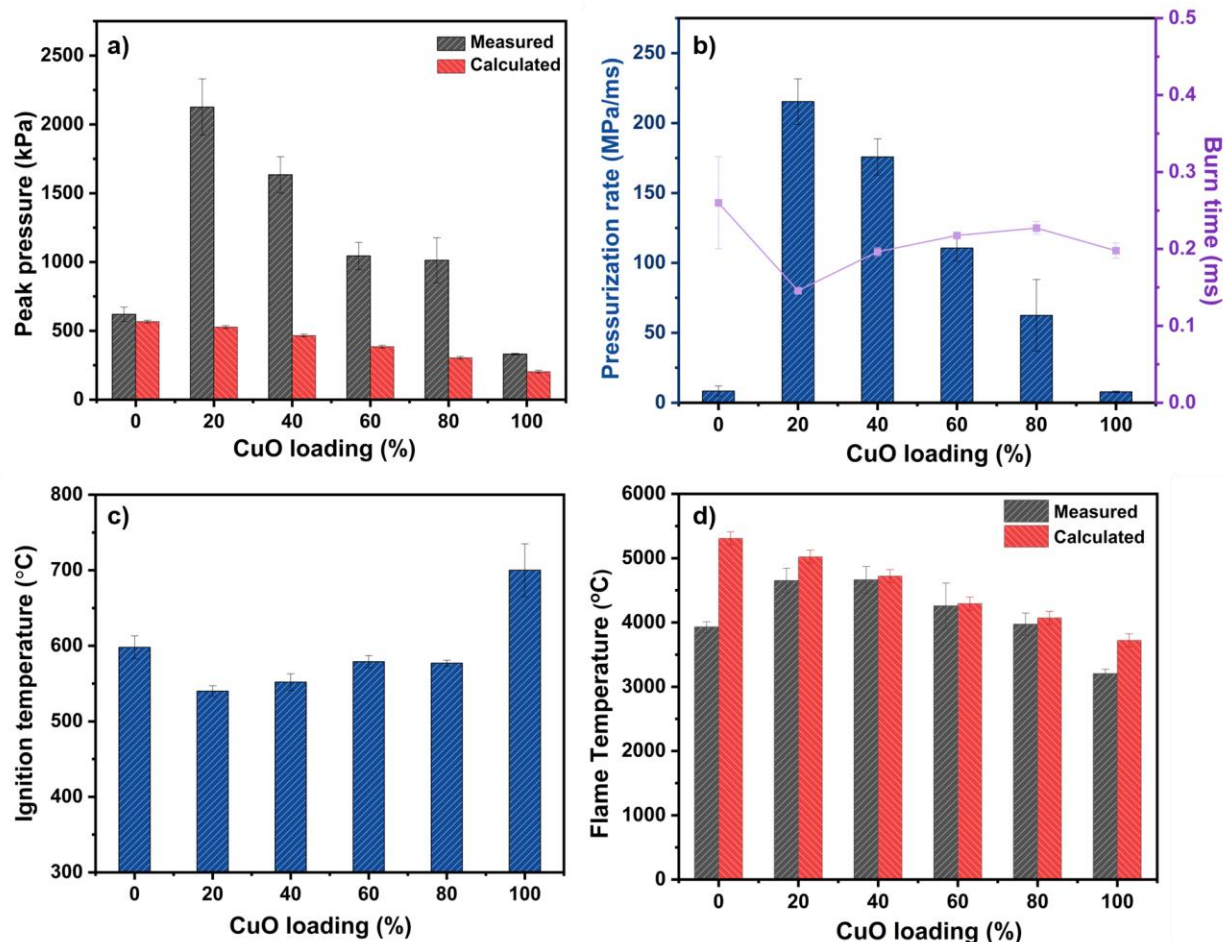


**Figure 2.** Temporal pressure traces of different Al/I<sub>2</sub>O<sub>5</sub>/CuO thermite powders.

The ignition temperature of all thermite powders characterized by T-Jump at a heating rate at  $\sim 5 \times 10^5$  C.min<sup>-1</sup> and under vacuum is plotted in **Figure 3c**. All ternary Al/I<sub>2</sub>O<sub>5</sub>/CuO

thermites ignite at a temperature slightly lower than that of Al/I<sub>2</sub>O<sub>5</sub>. Again, Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20% features the lowest ignition temperature, 540 °C.

Next, the average flame temperatures obtained by color ratio pyrometry following a previously published method [39] are plotted in **Figure 3d**, along with the adiabatic temperature calculated using Cheetah. The typical snapshots and corresponding flame temperature map of Al/I<sub>2</sub>O<sub>5</sub> are shown in **Figure S2** as an example. Al/CuO thermite has the lowest flame temperature in accordance with Cheetah 5.0 [3] thermochemical code (considering a total mass of 25 mg in a 20 cm<sup>3</sup> volume). However, all four Al/I<sub>2</sub>O<sub>5</sub>/CuO ternary thermites have either similar or higher flame temperature than Al/I<sub>2</sub>O<sub>5</sub>. Al/I<sub>2</sub>O<sub>5</sub>/CuO\_40% and Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20% thermites feature the maximum flame temperature (4650 °C), about 750 °C more than Al/I<sub>2</sub>O<sub>5</sub> at 3900 °C. It has to be noted that for more than 40% of CuO loading, the flame temperature decreases but remains hotter than those of Al/I<sub>2</sub>O<sub>5</sub> indicating that Al/I<sub>2</sub>O<sub>5</sub> succeed in maintaining a high temperature combustion regime even with only 20% of I<sub>2</sub>O<sub>5</sub> in the oxidizer. A more convincing result could be seen if we change the point of view to Al/CuO with I<sub>2</sub>O<sub>5</sub> addition. The flame temperature of Al/CuO jumps from 3200 °C to 4000 °C when only 20% of I<sub>2</sub>O<sub>5</sub> is incorporated into the system, confirming that the dominant thermite reaction is dominated between Al and I<sub>2</sub>O<sub>5</sub> which generates more heat than that of Al and CuO. Interestingly, in **Figure 3d**, whereas both binary thermite systems did not achieve their adiabatic flame temperatures probably due to incomplete reaction [39], all ternary systems feature flame temperatures much closer to their adiabatic temperature (<300 °C), the closest being obtained for Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20%.



**Figure 3.** Measured and calculated peak pressure (a), measured pressurization rate and burn time (b), ignition temperature (c), measured and calculated flame temperature (d), of Al/I<sub>2</sub>O<sub>5</sub> with different CuO loading.

As a summary of the ignition and combustion tests, addition of a strong oxidizer such as CuO into Al/I<sub>2</sub>O<sub>5</sub> thermites lead to promising new thermite composition featuring reduced ignition delays ( $\div 30$ ), shorter burn times ( $\div 2$ ), higher combustion temperatures (4650 °C against 3900 °C). We speculate that these new ternary thermite couples the advantage of each oxidizers. CuO due to its strong facility to release its oxygen at temperature as low as 477 °C [35,40], may impact the ignition of the Al fuel in the ternary thermite and might be responsible for the observed lower ignition delays and shorter burn times. While I<sub>2</sub>O<sub>5</sub> oxidizer

decomposition into gaseous  $I_2$  and  $O_2$  below 400 °C ensures a gas phase reaction producing high temperature combustion regime, i.e. above the vaporization of the products ( $Al_2O_3$ , Cu,  $I_2$ , etc.) and high-pressure development. To further study this speculation, we conduct two additional experiments.  $I_2O_5/CuO$  with different CuO loadings, and, then  $Al/I_2O_5/CuO$  thermites were analyzed by TGA/DSC at a heating rate of 10 °C.  $min^{-1}$  in Ar (**Figure 4**) with the goal to: (1) quantify the influence of CuO content on the  $I_2O_5$  decomposition process and onset; and, (2) quantify the influence of CuO on the nature of the low temperature exothermic events. For comparison, same experiments were conducted on  $Al/I_2O_5$  and  $Al/CuO$  powders.

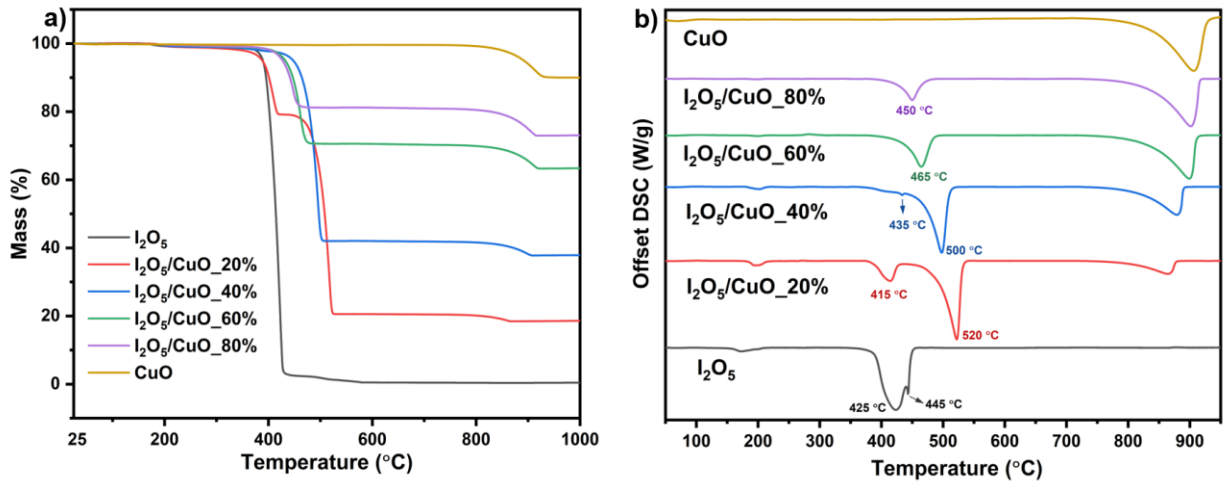
### 3.2. Influence of CuO on $I_2O_5$ decomposition

The  $I_2O_5$  decomposition undergoes the following two stages (black curves in TGA and DSC curves in **Figure 4**): a nearly negligible minor endothermic event located at around 200 °C corresponds to dehydration of  $HI_3O_8$  (a rehydrated product of  $I_2O_5$  during DSC preparation process due to its high hygroscopicity); the main endothermic event starting at 370 °C corresponds to the complete decomposition of  $I_2O_5$  into gaseous  $I_2$  and  $O_2$ . A small shoulder peak is spotted at around 450 °C along with the major endothermic peak in its DSC result. While, the TGA curve of  $I_2O_5$  indicates its complete decomposition in one step with an onset decomposition temperature at ~370 °C.

Both TGA and DSC results show that the CuO addition has nearly no influence on the first decomposition step of  $I_2O_5$  but rather pose significant impacts on the second endothermic event spanning from 350 to 550 °C based on the amount of CuO loading. With 20% CuO loading, the decomposition temperature of  $I_2O_5$  slightly decreases to 360 °C (red curve in **Figure 4a**), indicating a beneficial effect on the decomposition of  $I_2O_5$ . But the decomposition pauses at 420 °C and resumes again at 460 °C and finishes at 525 °C. The DSC result (red curve in **Figure 4b**) shows that the peak at 425 °C from neat  $I_2O_5$  shifted to a lower temperature at 415 °C; meanwhile the shoulder peak at 445 °C from bare  $I_2O_5$  shifted to

520 °C and separated from the main peak to appear as a single endothermic peak making the decomposition of  $I_2O_5$  into three steps. A similar phenomenon was also found previously by Pantoya et al [25] where an extra endotherm with a peak temperature at ~510 °C emerged after mixing  $Al_2O_3$  and  $I_2O_5$  together (with ~20 wt%  $Al_2O_3$  loading). They claimed that the exothermic binding process between the released gases and  $Al_2O_3$  brings the heat flow curve back to its baseline. Then upon the  $Al_2O_3$  phase change from amorphous to  $\gamma$  with an onset at ~480 °C, the absorbed  $I_2$  and  $O_2$  gases by  $Al_2O_3$  starts desorption and results in the emergence of the third endothermic event. It appears that CuO is functioning very similarly as  $Al_2O_3$  towards the decomposition behavior of  $I_2O_5$  here by separating its second decomposition step into two stages.

While 20% addition of CuO demonstrates weak positive influence on decomposition of  $I_2O_5$  by reducing its onset decomposition temperature by only 10 °C, higher CuO loadings on the contrary pose negative impact by increasing the  $I_2O_5$  onset decomposition temperature from 370 °C to temperatures higher than 420 °C as shown in **Figure 4a** and **Table 2**. The DSC results (**Figure 4b**) also show that the endothermic peak at 425 °C from neat  $I_2O_5$  moves to higher temperatures when CuO addition is more than 20%. It appears that only a small portion of CuO can facilitate the decomposition of  $I_2O_5$  and in fact excess CuO even slows down  $I_2O_5$  decomposition. Such results explain why Al/ $I_2O_5$ /CuO\_20% exhibits the best ignition performance than the other ternary systems (**Figure 3**); however, it still does not account for the significant enhancement of Al/ $I_2O_5$  combustion when CuO is added.



**Figure 4.** TGA (a) and DSC (b) results of  $I_2O_5$ ,  $I_2O_5/CuO_{20\%}$ ,  $I_2O_5/CuO_{40\%}$ ,  $I_2O_5/CuO_{60\%}$ , and  $I_2O_5/CuO_{80\%}$ . TGA/DSC experiments were performed in argon at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ .

**Table 2.** Onset decomposition temperatures of the  $I_2O_5$  decomposition from TGA experiments of  $I_2O_5$ ,  $I_2O_5/CuO_{20\%}$ ,  $I_2O_5/CuO_{40\%}$ ,  $I_2O_5/CuO_{60\%}$ , and  $I_2O_5/CuO_{80\%}$ .

	Onset decomposition temperature ( $^\circ\text{C}$ )
$Al/I_2O_5$	370
$I_2O_5/CuO_{20\%}$	360
$I_2O_5/CuO_{40\%}$	430
$I_2O_5/CuO_{60\%}$	420
$I_2O_5/CuO_{80\%}$	420

As addition of CuO into  $I_2O_5$  leads to a slight increase in the  $I_2O_5$  decomposition onset (except at 20% loading), it is not possible to explain the low ignition delay and faster burn rate of  $Al/I_2O_5/CuO$  thermites by considering only chemical and physical transformations. Next, we quantify the influence of CuO on the nature of the low temperature exothermic events of the ternary systems. For comparison, same experiments were conducted on  $Al/I_2O_5$  reference thermite.

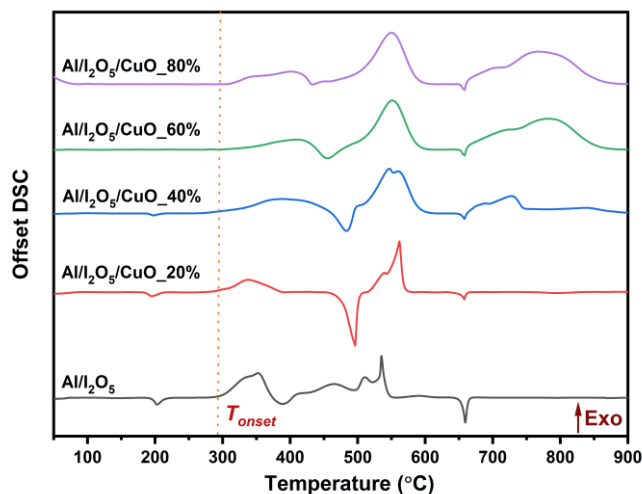


### 3.3. Influence of CuO on Al/I<sub>2</sub>O<sub>5</sub> low temperature reactions

Different from the two-stepped decomposition of I<sub>2</sub>O<sub>5</sub>, the DSC curve of Al/I<sub>2</sub>O<sub>5</sub> features a more complex pathway as shown in **Figure 5** (blue curve) due to the exothermic redox reactions. Begins with a small endotherm at ~200 °C corresponding to the dehydration of HI<sub>3</sub>O<sub>8</sub> similar to I<sub>2</sub>O<sub>5</sub>. Then a major exothermic event with an onset temperature at ~300 °C caused by the oxidation of aluminum by oxygen from I<sub>2</sub>O<sub>5</sub>. A previous study [41] has demonstrated that annealing aluminum-based thermites at temperatures > 200 °C could trigger modification of the Al/oxidizer interface chemistry that shorten the diffusion length between aluminum core and oxidizers and thus facilitate the ignition process, which might explain the low onset temperature of the first exothermic Al/I<sub>2</sub>O<sub>5</sub> reaction. Then the oxidation of aluminum event slows down by the endothermic event corresponds to the major decomposition of I<sub>2</sub>O<sub>5</sub>, which peaked at a slightly lower temperature than neat I<sub>2</sub>O<sub>5</sub>. With more I<sub>2</sub>O<sub>5</sub> decomposition, the exothermic oxidization of aluminum continues and mark its DSC curve with multiple exothermic peaks spanned from 400 to 600 °C. And the third decomposition peak of I<sub>2</sub>O<sub>5</sub> caused by the interaction between alumina and decomposition products I<sub>2</sub> and O<sub>2</sub> gases is also present in the case of Al/I<sub>2</sub>O<sub>5</sub>. Then the melting event of unreacted aluminum indicates the incomplete oxidization of aluminum.

Looking into the ternary systems, the top four curves in **Figure 5**, it seems that they all appear to undergo similar thermal events except for Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20% case. The first exothermic event of Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20% has the same onset temperature (~300 °C) as Al/I<sub>2</sub>O<sub>5</sub>; however, such temperature increases gradually with higher CuO loading and reached a plateau at 40% CuO loading (330 °C). When there is more than 40% of CuO loading in the ternary system, the onset of the Al/I<sub>2</sub>O<sub>5</sub> reaction is slightly delayed to a higher temperature at low heating rate condition. In addition, no more exothermic event is found after 600 °C for the case of Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20%, indicating that the thermal activities of Al/I<sub>2</sub>O<sub>5</sub>/CuO\_20%

finishes within a much smaller temperature range than the other systems in this work. Therefore, at low heating rate, Al/I<sub>2</sub>O<sub>5</sub>/CuO<sub>20%</sub> features equivalent onset temperature and shorter reaction duration in comparison to Al/I<sub>2</sub>O<sub>5</sub> redox reaction.



**Figure 5.** DSC results of I<sub>2</sub>O<sub>5</sub>, I<sub>2</sub>O<sub>5</sub>/CuO<sub>3%</sub>, Al/I<sub>2</sub>O<sub>5</sub>, and Al/I<sub>2</sub>O<sub>5</sub>/CuO ternary systems.

DSC experiments were performed in argon at a heating rate of 10 °C.min<sup>-1</sup>.

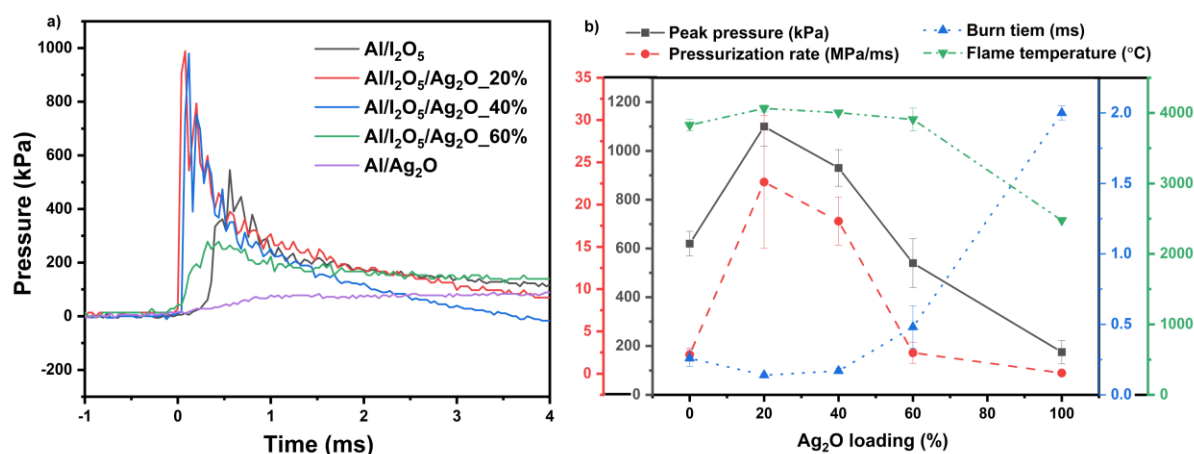
DSC analyses of ternary thermites confirms that the incorporation of 20% of CuO into Al/I<sub>2</sub>O<sub>5</sub> provokes a slight decrease in the I<sub>2</sub>O<sub>5</sub> decomposition onset and more complete reaction, but they fail in disclosing the mechanisms at the origin of this reduced ignition delay. Can it be caused by a catalytic effect provoked by chemical interactions between the two oxides? I<sub>2</sub>O<sub>5</sub>/CuO physically mixed oxides were examined by FTIR (**Figure S3**) and no noticeable change of the CuO and I<sub>2</sub>O<sub>5</sub> spectra were found which confirms that no chemical interaction occurs between the two oxidizers at ambient. Last likely cause of the very short ignition delay is a modification of the thermal properties of the thermite mixture when adding CuO into the Al/I<sub>2</sub>O<sub>5</sub>.

### 3.4. Discussion on the role of thermal properties on the ignition delay

The ignition of the ternary thermite is performed by Joule heating as loose powders “enrobe” a thin Nichrome wire. In this heating configuration, evidently, the thermal

properties of the thermite material play a critical role in the diffusion of the heat from the hot wire to the thermite. This can explain the difference in the ignition delay between Al/I<sub>2</sub>O<sub>5</sub> and Al/CuO. The material with higher thermal conductivity will show a shorter ignition delay [42]. The thermal conductivity of nanosized CuO is ~30 W.m<sup>-1</sup>.k<sup>-1</sup> [43,44]. Unfortunately, such data is not available for I<sub>2</sub>O<sub>5</sub> in the literature. Thus, as - according to Wiedemann–Franz law - the thermal conductivity is positively correlated to the electrical conductivity, we propose to make an evaluation of thermal conductivity trend between I<sub>2</sub>O<sub>5</sub> to CuO oxidizer based on the electrical properties. Both oxides were pressed into coin pellets (~0.5 mm in thickness) before resistivity measurement. At the ambient, the sheet resistance of CuO is measured at ~550 kΩ/□; where I<sub>2</sub>O<sub>5</sub> has a sheet resistance even exceeds the tool range to be gauged; i.e., CuO is a much better electrical conductor than I<sub>2</sub>O<sub>5</sub>. So that we can deduce that CuO is a better thermal conductor than I<sub>2</sub>O<sub>5</sub>. Hence, replacing some I<sub>2</sub>O<sub>5</sub> oxide by CuO improves the overall powder thermal conductivity and helps thermal transfer from the hot wire and within the thermites. This simple reasoning helps us to understand why ternary thermite has a shorter ignition delay and shorter burn time as well. This was verified by a last experiment : 20%, 40%, and 60% addition of Ag<sub>2</sub>O particles having the same dimension as CuO particles and featuring a slightly lower thermal conductivity (~25 W.m<sup>-1</sup>.k<sup>-1</sup>) [45] is added to Al/I<sub>2</sub>O<sub>5</sub> thermite and tested in ignition and combustion under the same conditions. As shown in **Figure 6**, Ag<sub>2</sub>O addition shows almost the same effect as CuO addition on ignition delay and burn time, increasing peak pressure and pressurization rate, and meanwhile maintaining the high flame temperature of Al/I<sub>2</sub>O<sub>5</sub>, except for the scale of the enhancements by Ag<sub>2</sub>O addition is much weaker than the case of CuO. It makes sense since Ag<sub>2</sub>O is a much weaker oxide than CuO in aluminum-based thermites based on previous reported work [46–48]. Thus, it is reasonable to assume that adding a secondary metal oxide that features a good

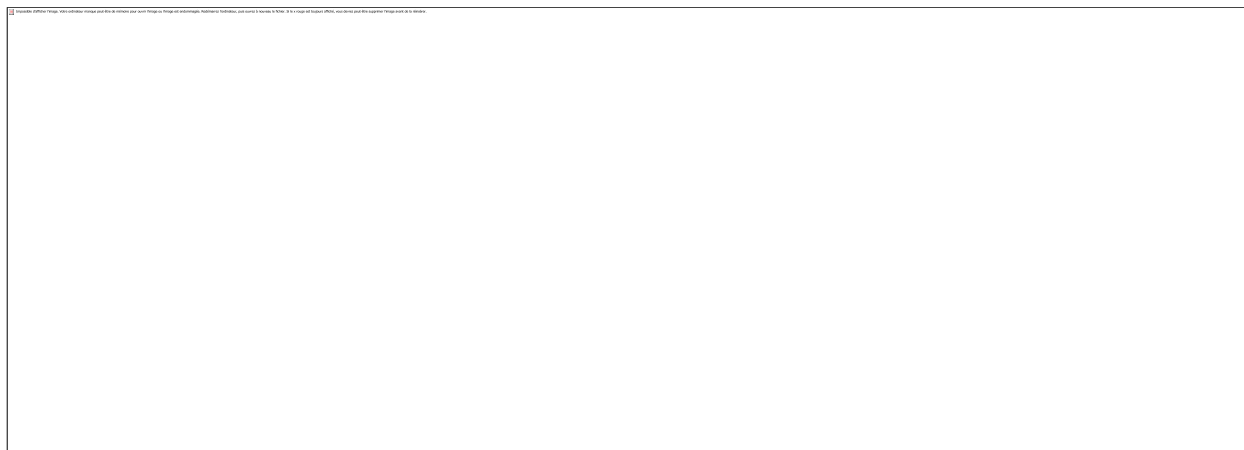
thermal conductivity into Al/I<sub>2</sub>O<sub>5</sub> thermitic can extensively boost its overall combustion performance in a constant volume combustion cell.



**Figure 6.** Temporal pressure traces (a) and combustion performance (b) of different Al/I<sub>2</sub>O<sub>5</sub>/Ag<sub>2</sub>O thermites.

### 3.4. Reaction mechanisms of Al/I<sub>2</sub>O<sub>5</sub>/CuO

From all aforementioned characterization results and analyses we can propose a reaction mechanism of Al/I<sub>2</sub>O<sub>5</sub>/CuO (**Figure 7**). Al/CuO ignites readily upon triggering by Joule heating. The generated heat/energy then ignites the adjacent Al/I<sub>2</sub>O<sub>5</sub>. The high reaction temperature from Al/I<sub>2</sub>O<sub>5</sub> facilitates the further decomposition of the remaining oxidizers, which in turn accelerates the aluminum oxidation by providing large amount of oxygen and leads to a shorter burn time. Thus, the additive CuO shortens the ignition delay of Al/I<sub>2</sub>O<sub>5</sub> but also -being a strong oxidizer- release a high amount of gaseous oxygen for aluminum to react. In parallel, the very high flame temperature of the Al/I<sub>2</sub>O<sub>5</sub> reaction occurring in gaseous phase further boosts the pressure. High temperature and high oxygen content result in a shortened pressure pulse of high amplitude and rate accelerate the overall reaction. All those events occur simultaneously within 0.15 ms, so that we can conclude as a synergistic effect of both oxidizers which enhances the ignition and combustion performance of Al/I<sub>2</sub>O<sub>5</sub> in a closed volume environment.



**Figure 7.** Schematics of the boosting mechanism of Al/I<sub>2</sub>O<sub>5</sub> combustion with CuO addition.

#### **4. Conclusions**

A secondary oxidizer CuO was incorporated into Al/I<sub>2</sub>O<sub>5</sub> system with the goal to shorten its ignition delay without penalizing their combustion performance (pressure development). Four different Al/I<sub>2</sub>O<sub>5</sub>/CuO thermites with varying oxidizer mass ratios were characterized in ignition and combustion in a constant volume combustion cell. The four ternary thermites feature higher peak pressures, pressurization rates, flame temperatures and shorter ignition delay than that of Al/I<sub>2</sub>O<sub>5</sub>. Multiple characterization tools were used to identify the cause of such improvement. FTIR analysis show no surface interaction between the two oxides. TGA/DSC results show that CuO addition has limited influence on the decomposition of I<sub>2</sub>O<sub>5</sub> and on the reaction of Al/I<sub>2</sub>O<sub>5</sub>. However, it has been verified in this work that CuO has a much better thermal conductivity than I<sub>2</sub>O<sub>5</sub>, which improves the thermal transfer within the Al/I<sub>2</sub>O<sub>5</sub>/CuO thermites and thus creates a positive effect on its combustion. Finally, a reaction mechanism could be proposed for Al/I<sub>2</sub>O<sub>5</sub>/CuO to explain this unexpected improvement. This work not only proposed a new high performing biocidal energetic material containing 80/20 wt% of I<sub>2</sub>O<sub>5</sub>/CuO but also unravel the reasons of ignition and combustion performances enhancement for potential applications.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://>

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