

Study on Thermal Behaviour of AP/LiBH₄ Energetic System

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Abstract: Ammonium perchlorate (AP) and LiBH₄ can form an oxidation-fuel energetic system, which provides a new development direction in designing novel mixed explosive formula. The microcalorimetry and self-designed slow cook-off setup were used to study thermal performance of AP/LiBH₄ energetic powders and grains respectively. Experimental results show that heat release in micro-

calorimetry method for the mixed system at low temperature was due to the reaction between LiBH₄ and residual water vapour. The oxidant gases from AP decomposition participate in the oxidation of LiBH₄ at high temperature. The ignition temperature for the AP/LiBH₄ grain was 270 °C and the explosion reactions were violent in slow cook-off test.

Keywords: AP · LiBH₄ · energetic system · mixed explosive · thermal behaviour

1 Introduction

Currently, there has been an increasing demand for exploring high energy explosive to adapt to the development of ammunition technology. However, the direct preparation of single explosive is confronted with more and more technical difficulty. On the contrary, mixed explosive has proved a key approach to improve explosion energy by designing and exploring oxidant-fuel energetic systems, and represents an important research direction of weapon systems [1–5]. Owing to the strong reactivity and high combustion heat, metal hydrides attract great attention as candidates of fuel additives in energetic system for several decades. In the last century, Matzek [6] and Flynn et al [7] carried out the work on the application of metal hydrides as energetic materials respectively. These studies indicated that higher energetic density and lower flame temperature were achieved due to a lot of heat and light gaseous products by adding metal hydrides in propellants. Based on Hradel's research [8], addition of magnesium hydride (MgH₂) in explosives could improve the total work capacity. By comparing the influence of aluminum, magnesium and their hydride powders on the properties of nitramine explosives and pyrotechnics, Selezenev and Ward [9,10] concluded that the explosion characteristics in the compositions with hydride powders were superior to that with metal powders. Cheng et al [11] introduced MgH₂ to emulsion explosives and found that MgH₂ plays a dual role as a sensitizer and an energetic material. As a hydrogen storage material with the largest hydrogen gravimetric density, LiBH₄ has a strong chemical reactivity and is able to provide great heat of combustion, which is expected to be a candidate of high-energy combustible agent. However, few literatures about LiBH₄-containing energetic system are published.

High density compound ammonium perchlorate (AP) is known as the representative oxidant with outstanding comprehensive properties and widely application in propellants,

explosives and pyrotechnics [12]. So AP and LiBH₄ may form a typical oxidation-fuel energetic system.

Most of the physical and chemical reactions are accompanied with heat release process which in turn characterizes chemical reactions. Microcalorimetry is used to measure the latent heat release during the decomposition process of a small amount of energetic system at different temperatures and it also has received application in explosives, gunpowder, pyrotechnics etc [13–16]. The cook-off experiment is an important method in estimating thermal stability of explosive formula [17]. There are considerable researches on cook-off thermal explosion experiments of traditional explosives [18–22]. In the present paper, thermal behaviors of AP/LiBH₄ mixture and the individual component were investigated by both microcalorimetry and slow cook-off test.

2 Materials and Methods

2.1 Materials

The LiBH₄ used in the experiment was purchased from Alfa Aesar Company (St. Paul, MN, USA). The purity was 95% with average particle size about 10–20 μm. AP was synthesized by Xi'an Modern Chemistry Research Institute with particle size of 10–20 μm. For AP, LiBH₄ and the mixed sample of AP/LiBH₄, coating processing was implemented to avoid the air pollution by the same inert binder [23] (wax

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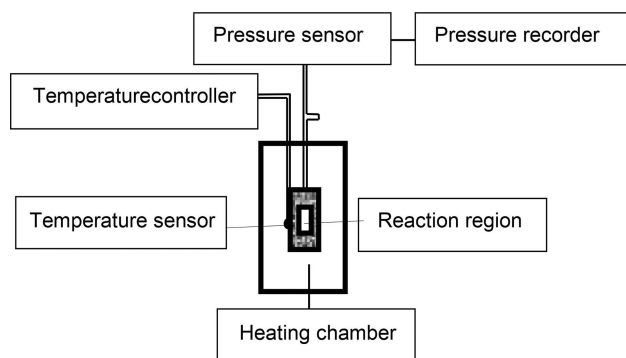


Figure 2. Experimental set up of cook-off test.

and polyester carbonate) (5 wt.%) in both microcalorimetry and cook-off tests. The hydride compounds were prepared, coated and loaded into the experimental equipments (microcalorimeter and cook-off pot) in or transferred from a glove box with the humidity 200 ppm (0.0002%).

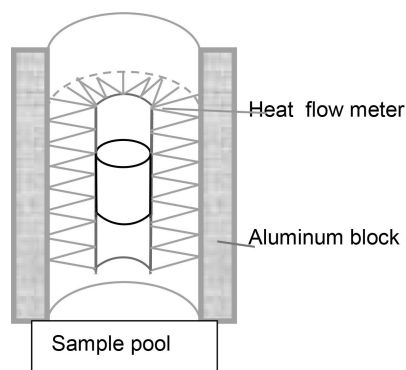


Figure 1. Structural composition of heat flow calorimeter.

2.2 Microcalorimetry Method

The C80 heat flow calorimeter by Setaram Instrumentation Company (France) was used in the experiment. The schematic diagram is shown in Figure 1. The samples were heated from 30 °C to 100 °C at 6 °C/h and then were maintained at 100 °C for 50 h. Considering the possible chemical danger and other uncertainty for the new energetic system, 20 mg AP/LiBH₄ (at the mass ratio of 1:1) mixed powders and each

Table 1. Sample formulas in cook-off tests.

Samples	w(AP)%	w(LiBH ₄)%	w(binder)%	Pellet size [mm]
1#	95	0	5	Ø20 × 30
2#	0	95	5	Ø20 × 30
3#	90	5	5	Ø20 × 30

individual component in 10 mg were tested respectively. The experimental power-time curve for the AP/LiBH₄ mixture in 300 mg was compared with the hypothetical curve constructed from the results of AP and LiBH₄ in 150 mg.

2.3 Cook-off Test

In the present research, the small-scale AP/LiBH₄ pellet was prepared and the responding condition was studied at several temperatures so as to provide a technical support for the storage and safe application of AP/LiBH₄. Table 1 shows the details of samples used in the cook-off test.

The cook-off experimental device was designed and installed as the schematic shown in Figure 2.

The experimental system consisted mainly of a heating cylinder shell with a topcap, a temperature thermocouple, a pressure sensor and a pressure recorder. Shell materials were all composed of general 1045 carbon steels. The cylinder had a 20.2 mm inner diameter, 30.3 mm length, and 2.5 mm wall thickness. The length-diameter ratio of the cylinder was about 1.5, which was similar to practical usage. The pressed samples was fixed and heated in the chamber. The maximum clearance between explosive sample and inner diameter of the shell was 0.2 mm, and the clearance in height was not greater than 0.3 mm. The furnace offered thermal power for the cook-off samples. When the temperature reached the set value, it was maintained and adjusted constant by PAD27 modulator. The temperature outside the cylinder throughout the heating process was measured by a Ni–Cd/Ni–Si thermocouple fixed at the center of the cylinder's exterior with heat-resistant material. The design and installation of heating furnace wire board can guarantee the uniformity of temperature field in the furnace. The heating rate was set by temperature controller typed MRI3 (The precision of temperature control is plus or minus 12 °C/h). The pressure sensor in the middle of the topcap was used to measure the actual gaseous pressure. The temperature and pressure were continuously tracked while a temperature–time curve and a pressure–time curve were recorded respectively.

In consideration of experimental risk, the heating rate was set as 3.3 °C/h initially to avoid a sudden exotherm and then it was controlled at 60 °C/h after the temperature reached 60 °C. Samples AP, LiBH₄ and AP/LiBH₄ grains were heated in the above device and all stayed isothermal at 60 °C, 100 °C and 180 °C for 5 h in their heating process to investigate the responding state of samples respectively. Curves of temperature–time and pressure–time were obtained from the research on the decomposition characteristics of the three samples. Two parallel tests were performed for each component in the similar condition. Followings are the details of experimental conditions in Table 2.

Table 2. Details of temperature condition.

Temperature [°C]	Heating rate [°C h ⁻¹]	Time [h]
< 60	3.3	/
60	/	5
60 ~ 100	60	0.67
100	/	5
100 ~ 180	60	1.33
180	/	5
180 ~ 400	60	/

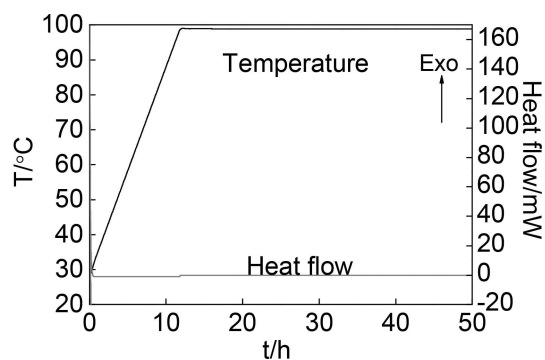
3 Results and Discussions

3.1 Thermal Behaviour of AP/LiBH₄ Powder

Figure 3 shows the temperature-time and heat-time curves of three heated energetic samples. According to the literature [24], AP commences an exothermic decomposition at more than 230 °C generally. As Figure 3(a) shows, no significant heat release is observed below 100 °C for AP. There is also no crystal transformation of AP powder occurred. Heat flow curve for 10 mg LiBH₄ is flat with increasing of time and temperature. However, when LiBH₄ mass increases to 150 mg, the heat release is clear (Figure 3(b)).

LiBH₄ usually crystallizes with an orthorhombic structure in a tetrahedral configuration at normal temperature and crystallizes with a hexagonal structure at high temperature [25–29]. The exothermic characteristics for LiBH₄ in Figure 3(b) were also found by Lang et al [30] who attributed it to the phase transition from the low temperature to high temperature. They concluded that the exotherm was due to hydrogen release from a solid solution of LiBH₄ at low temperature phase, but was not caused by air contamination. A slight hydrogen desorption of 0.3 to 1.3 wt.% was observed during the structural phase transformation process [31,32]. However, the LiBH₄ studied in the research was used under 2×10^5 Pa of hydrogen with a 20 °C/min ramp. Therefore, their conclusion needs more discussion in details. Without further evidence, air contamination is still believed as the main approved interpretation in our test. In fact, the effect of the air for LiBH₄ is proved to be hard to neglect in many studies [33–35].

The exothermic characteristics for the samples containing 150 mg LiBH₄ are listed in Table 3. Two exothermic peaks are observed in Figure 3(b) and (d). The beginning and end temperatures of transition are given while the values in parentheses are peak temperatures. Table 3 presents also the first exothermic peak temperature at the heating process while the second peak appears at the isothermal stage. Mixed AP/LiBH₄ presents different heat-time curves with different loads in Figure 3(c) and 3(d). It shows that no heat fluctuating is observed in the experiment for AP/LiBH₄ with the loading of 20 mg, while a remarkable but small exothermic peak emerges for 300 mg AP/LiBH₄ in the heating process. However, there is no significant difference be-



(a) AP-10mg

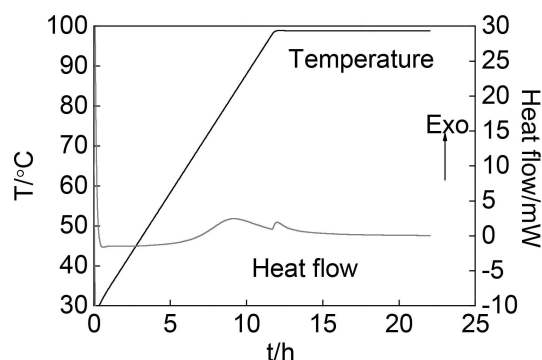
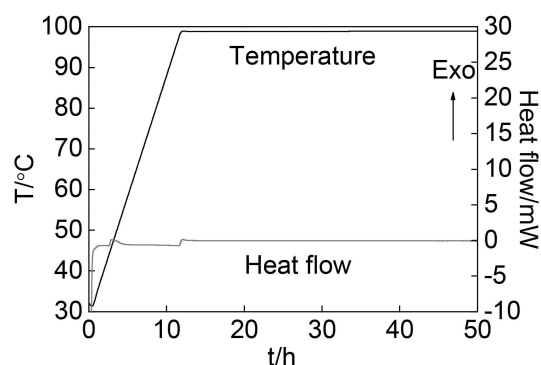
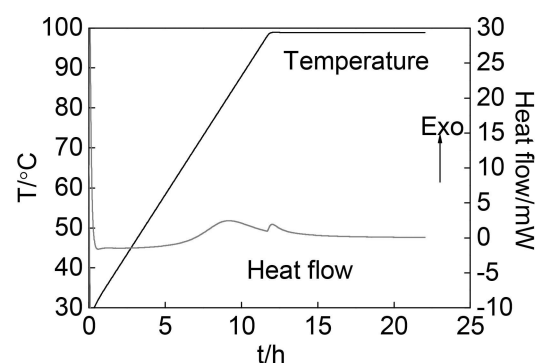
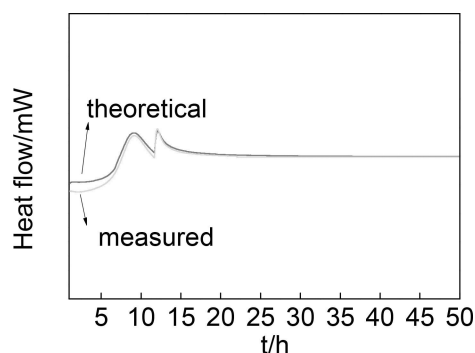
(b) LiBH₄-150mg(c) AP-10mg/LiBH₄-10mg(d) AP-150mg/LiBH₄-150mg**Figure 3.** The curves of heat flow and temperature of samples.

Table 3. The exothermal characteristics of samples.

Samples	M [mg]	T ₁ (T _{1p}) [°C]	T ₂ (T _{2p}) [°C]	Heat released [kJ kg ⁻¹]
LiBH ₄	150	64.31 ~ 97.93 (81.83)	97.94 ~ 98.94 (98.94)	−295.04
AP/LiBH ₄	300	59.72 ~ 97.83 (81.33)	97.82 ~ 98.93 (98.93)	−147.45

tween two T-t curve trends. It presents that the powder experiences a negligible heat reaction between LiBH₄ and AP in the test. The exothermic reaction is observed for AP/LiBH₄ powder before it reaches 100 °C. The initial exothermic reaction of AP/LiBH₄ sample initiates at 59.72 °C and the reaction reaches its peak (T_{1p}) at 81.33 °C. Compared with individual LiBH₄ which reacts at 64.31 °C and reaches its peaks at 81.83 °C, mixed powder releases heat in advance a little.

By integrating heat flow with time, we obtained the total heat release (area under the curve) in the reaction. The cumulative heat release of AP/LiBH₄ is available (−147.45 kJ/kg at 98.93 °C) as half of that of LiBH₄ component. The theoretical heat flow is deduced as the sum of that for each component. Comparative analysis between theoretical heat release and measured values is conducted, which displays two nearly overlapping curves in Figure 4. These results confirm that LiBH₄ principally participates at the low temperature stage reaction below 100 °C, and the heat release may result from the hydrolysis reaction of LiBH₄.

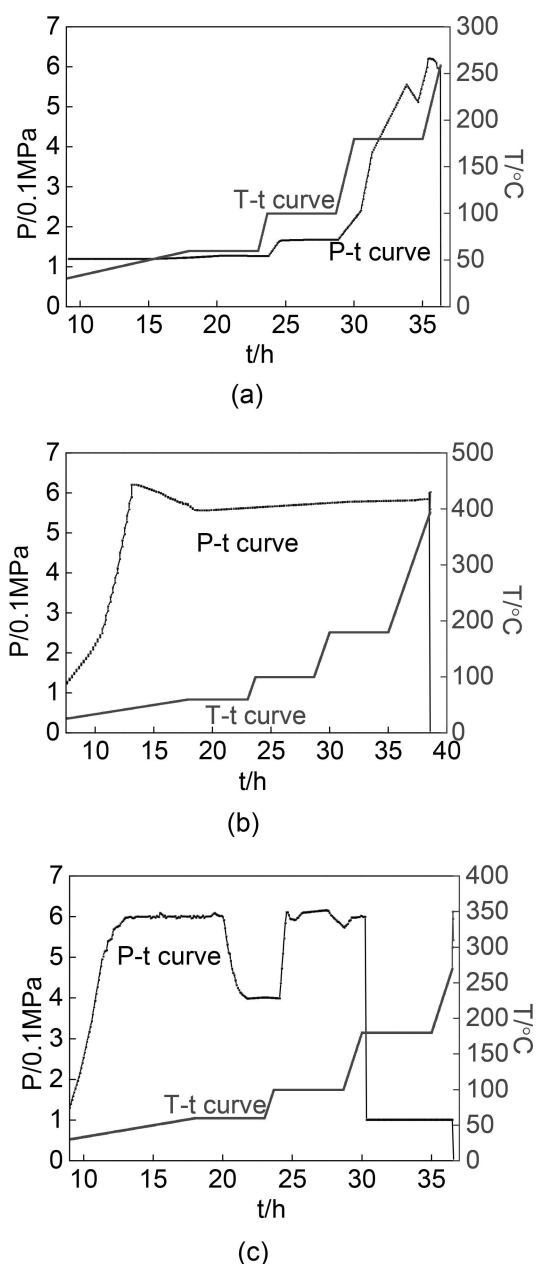
**Figure 4.** The curves of measured and theoretical heat flow of AP/LiBH₄.

Based on the analysis, the stability of AP/LiBH₄ sample in small scale is preferable and the compatibility is acceptable.

3.2 Thermal Behaviour of AP/LiBH₄ Grain

This cook-off experiment was conducted to simulate the thermal environment for AP/LiBH₄ grain and to detect the

response sensitivity and the violence extent. The response mechanism of nonhomogeneous explosive can be explained by hot ignition and hot spots theory [36]. In heating process, hot spots form and the grain thermally decomposes [37]. High-temperature gaseous products present a continuous release and induce a pressure improvement of inner grain which may further result in a deflagration or detonation [38]. Generally there is no phase transition in the cook-off test [39]. Figure 5 shows how gaseous pressure changes with temperature in the closed chamber. The abrupt temperature rises on the end of T-t curve in Figure 5

**Figure 5.** P-t curves and T-t curves of samples heated slowly: (a) AP; (b) LiBH₄; (c) AP/LiBH₄.

and the values in Table 4 depict the response characteristics undergoing a severe reaction.

Table 4. Measured spot temperatures and case distortion.

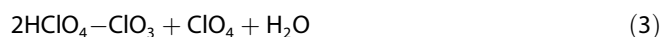
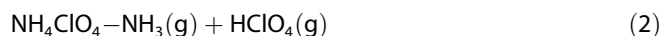
Samples	Temperature [°C]	Time [h]	Response
1#	259	36.3	detonation
2#	393	38.5	deflagration
3#	270	36.5	detonation

The damage degree of the shell serves as the basis of judging detonation or deflagration in the experiment [40]. When it undergoes a process of deflagration, the grain burns and leaves some residues while the shell keeps intact. If the increasing gaseous pressure far exceeds the shell yield strength (Eq. (1)) and severely damages the shell in little pieces, the response detonation response happens.

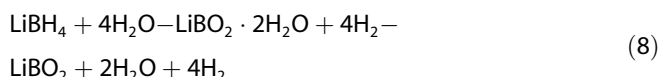
$$p = a/c \cdot dp/dt + p^* \quad (1)$$

Where p is the instant pressure at explosion, dp/dt is rate of gaseous pressure, p^* is yield strength of the shell, a is charge size and c is sound velocity.

As Figure 5(a) shows, the pressure remains constant at the first heating stage below 60 °C while a slow pressure increment occurs at 60~100 °C heating process. Decomposition of pure AP commences at 180 °C isothermal stage while the pressure increases fast in enclosed environment. It refers to a comprehensive connection consisting of hundreds of chain reactions. According to the literature [41,42], NH₃ and HClO₄ are generated firstly via proton transference for AP decomposition at low temperature (Eq. (2)). At the end of this isothermal stage, the pressure undergoes a rapid increment to 0.55 MPa at 28 h. Through a series of degradation reactions of HClO₄ in gaseous state intermediates ClO₃, ClO, O and H₂O are likely to be generated (Eqs. (3~5)) [43]. The following temporary decrement of pressure is possibly attributed to the reduction of gaseous molecules. On the one hand, NH₃ is most likely to be oxidized by O radicals among all the oxidant products from HClO₄ which results in the reducing of gaseous molecular number (Eq. (6)); on the other hand, the residual NH₃ covers the surface active site of AP crystal and restrains the further decomposition at low temperature [43]. At higher temperature, the reaction center gets activated again due to desorption of NH₃ and more gaseous products. The pressure increases rapidly to 0.6 MPa and the grain explodes in fragments.



The P-t curve of LiBH₄ grain (Figure 5(b)) suggests that the gaseous pressure raises rapidly in the first heating period and it reaches 0.25 MPa at 10.9 h when the temperature is 39.5 °C. However, according to former research [36], LiBH₄ decomposes thermally and realizes hydrogen gas at phase transition stage (about 100~110 °C, first stage), melting point (about 260~280 °C, second stage) and decomposition stage (375~547 °C, third stage). Most of the hydrogen will be produced at the third stage. The reason of hydrogen release at so low temperature is not yet fully understood, but the possible scenarios might be addressed as by the analysis for microcalorimetry experiment. In our test, it is impossible for LiBH₄ decomposition at such a low temperature; it can be only explained by the reaction of LiBH₄ with water vapour. Actually, it has been shown in some literature [33,34] that LiBH₄ can react with moisture to form LiBH_x(OH)_y phases in Eq (7), which release hydrogen at low temperature. Our former research shows that such borohydride oxidation could be responsible for the low temperature hydrogen release in Eq. (8) [44], and the occurrence of some irreversible reactions between LiBH₄ and hydroxyl groups (or other oxygen-containing groups) at the micropores surface could also explain this huge change of thermodynamic behaviour. The maximum pressure is 0.6 MPa at 13.7 h when the sample is at 48.5 °C. There is the station equation of ideal gas which is applicable for gases in low pressure less than several atmospheric pressures. The V and R are constant in the experiment, so the pressure is directly proportional to the number of gas molecules at certain temperature. In the retrained and enclosed condition, pure LiBH₄ grain initiates an exothermic decomposition at 393.6 °C in this experiment. Exploding occurs to the sample accompanied with the abrupt temperature rise from 393 °C to 400 °C. After the experiment, the shell keeps its general integrity while only some black residuals are attached to the shell wall, which proves a deflagration reaction happens.



There are many common characteristics for the foregoing section in P-t curve of LiBH₄ and mixed grain. The gaseous pressures both reach a very high value. The difference is that, the pressure for AP/LiBH₄ grain presents a sudden decrement following a several-hour high value. The self-ignition temperature for the sample AP/LiBH₄ is 270 °C (Figure 5(c)). A severe reaction happens earlier than AP sample and the shell is seriously damaged. Thermal explosion

response is an incompatibility issue between LiBH_4 and AP and mainly due to the thermal reaction of AP.

We can interpret our results on the basis of the hypothesis that there are generally two possible stages for AP/ LiBH_4 grain in the cook-off reaction process. H_2O has priority in oxidizing LiBH_4 over AP. At low temperature, LiBH_4 reacts with the water vapor and release a large quantity of gas while AP keeps thermally stable. Onset temperature for AP decomposition appears during 100–180 °C heating process. Transient redox reaction of AP/ LiBH_4 replaces hours of decomposition of AP and ends with a more severe damage response at a lower temperature at 270 °C.

4 Conclusion

- (1) No significant heat release was observed when AP and LiBH_4 mixed in powder state below 100 °C in minimal scale in micro calorimetry test. The 150 mg AP remained thermally stable while LiBH_4 in equal quantity started an exothermic hydrolysis reaction. As a whole, AP/ LiBH_4 powder system does not release more heat than the sum of each component.
- (2) The ignition temperature obtained in slow cook-off test for AP/ LiBH_4 grain was 270 °C. Thermal explosion response was an incompatibility issue between LiBH_4 and AP and mainly due to the thermal reaction of AP.
- (3) There is a complex chemical reaction between LiBH_4 and AP. LiBH_4 is easily oxidized by H_2O in the energetic system and AP will act as the oxidizer for the reducing gases released from LiBH_4 . The synchronization of reaction for AP and LiBH_4 in energetic system is expected which means the stability of LiBH_4 is badly in need.

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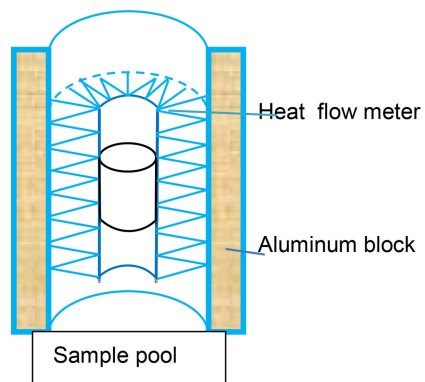
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1 – 8

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