

## CIEMAT experimental proposal on lithium ignition in support of DONES licensing (LiFIRE facility)

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### ABSTRACT

In the DEMO-Oriented NEutron Source (DONES) facility, it is expected to use a considerable amount of lithium at an average temperature higher than 300 °C. It is well known that lithium can produce exothermic reactions with several media, generating corrosive and toxic (upon burning) reaction products and with the potential risk of mobilizing radionuclides in little amounts. As a result, lithium represents a hazardous material which must be safely handled under normal operation and, especially, potential accident conditions which involve lithium spills and radioactive releases.

Although the burning behavior of lithium has been studied for several decades, there is still a wide dispersion of data regarding its actual ignition temperature. Generally, measurements of the spontaneous or induced ignition temperature of a leakage of molten lithium, pool/spray type, depend on several factors such as metal purity, gas atmosphere composition and relative humidity, sample size or geometrical aspects, and even different treatments, apparatus, and techniques used.

A dedicated experimental facility, called "LiFIRE", is currently under development at the National Fusion Laboratory of CIEMAT with the purpose to quantitatively support the DONES safety analysis on the fire risk in case of lithium leakages, based on the Defense-in-Depth principle, i.e. prevention, detection and mitigation.

### 1. Introduction

The main lithium loop and circuits of the DEMO-Oriented NEutron Source (DONES) facility will contain around 10 m<sup>3</sup> of liquid lithium flowing at a temperature greater than 300 °C [1]. Although lithium is the least reactive of the alkali metals, it can undergo many chemical exothermic reactions [2–4]. In fact, it can readily react with oxygen, nitrogen, carbon dioxide, water and concrete, generating an important population of corrosive products, including lithium hydroxide, oxide, peroxide, carbonate, nitride and hydride, which, upon burning, are toxic and harmful for the respiratory system. These latter compounds must be handled with caution since they can potentially lead to undesirable secondary exothermic reactions. An example is the production of ammonia from the reaction between lithium nitride and water (i.e. Li<sub>3</sub>N + 3 H<sub>2</sub>O → 3 LiOH + NH<sub>3</sub>). Reaction of lithium with water can also produce an important quantity of hydrogen gas (i.e. Li + H<sub>2</sub>O → LiOH + 1/2 H<sub>2</sub>) with the consequent potential risk of explosions.

Moreover, in irradiation facilities like DONES, the radiological source term resulting from deuteron and neutron interaction with lithium (and other metallic elements), represented by the radionuclides carried by the flowing lithium inside the closed loops or retained in dedicated traps (e.g. H<sup>3</sup>, Be<sup>7</sup>), can be mobilized upon fire conditions [5].

Therefore, this alkali metal is considered a hazardous material to be safely handled during normal operation and, especially, under potential accident conditions involving lithium spills and contaminations, which may occur during the lifetime of the facility.

Following an extensive literature review, a considerable data dispersion regarding the ignition temperature of lithium in air has been found. Generally, measurements of the spontaneous or induced ignition temperature of a pool or spray of molten lithium depend on a given number of factors, such as: the metal purity, the oxidation on the metal surface, the composition and humidity of the reactant atmosphere, the sample size or geometrical aspects (e.g. metal surface available for reaction), the different sample treatments, and the experimental apparatus

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and techniques used. With the available data collected from literature, it is practically impossible to fix requirements for the DONES design that significantly limit the fire risk of the plant.

In this context, a dedicated experimental facility, called "LiFIRE", is currently being developed at the National Fusion Laboratory (LNF) of CIEMAT with the purpose to quantitatively support the DONES safety analysis on the fire risk in case of lithium leakages from the prevention, detection and mitigation points of view. The general scope of the LiFIRE experiments is to provide experimental evidences for demonstrating the fire protection requirements, which will have to be later on implemented in the engineering design of the DONES facility. These data will be of the utmost importance for its licensing in front of the Regulatory Body of nuclear and radioactive facilities.

## 2. Literature on molten lithium reactions with air

From a literature review on past R&D studies on lithium pools-air reactions, based on the amount of lithium used and size of the experimental facility, the following three main classes of experiments have been distinguished:

- small-scale experiments, where up to a few grams of lithium were used [6–9],
- medium-scale experiments, where the mass of the lithium samples was approximately between several tens up to a few hundred grams [10,11],
- and large-scale experiments, in which several kilograms of lithium were employed [2].

In general, regarding the ignition temperature of lithium in air, a large discrepancy between 180 °C (lithium melting point) and 640 °C is noted, mainly due to metal purity and air moisture conditions, according to [2,3]. Indeed, many past experiments were focused mainly on determining the reaction rate of the lithium combustion in air and on estimating the aerosols production. Moreover, data on the ignition temperature and on some initial experimental parameters (e.g., relative humidity, reaction surface area) were not always provided.

Examples from past experimental activities, in terms of initial conditions and ignition temperature of lithium in air, are provided in Table 1.

Since the main final products of the lithium combustion in humid air are LiOH, Li<sub>2</sub>O and Li<sub>3</sub>N, the exothermic reactions, collected in Table 2, with their respective heats of reaction (normalized per mole of lithium

**Table 1**  
Initial conditions and ignition temperature of lithium in air from past experimental activities.

Parameter	Small-scale experiments	Medium-scale experiments	Large-scale experiments
(Reference)	[6]	[9]	[11]
Lithium mass (g)	4	1.5	n/a (between 100 and 600 g)
Atmosphere composition nitrogen/oxygen (%)	n/a	79/21	80/20
Relative humidity (%)	0 (dry air)	52	n/a
Reaction surface area (cm <sup>2</sup> )	7	8	n/a
Lithium ignition temperature (°C)	443	451	316
			640
			400
			243

**Table 2**  
Heats of reaction of lithium-air reactions.

#	Reaction	Heat of reaction at 500 °C (kJ/molLi)	References
1	1Li + 1/4 O <sub>2</sub> → 1/2 Li <sub>2</sub> O	302	[2]
2	1Li + 1/6 N <sub>2</sub> → 1/3 Li <sub>3</sub> N	69	[2]
3	1Li + 1 H <sub>2</sub> O → 1LiOH + 1/2 H <sub>2</sub>	508.6 (at 25 °C)	[3]
4	(1Li + 3/4CO <sub>2</sub> → 1/2 Li <sub>2</sub> CO <sub>3</sub> + 1/4C)	318	[2]

reacted) were considered for the development of the preliminary design of the LiFIRE facility. The reaction involving lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) can be discarded from the rest of the lithium-air reactions, being the CO<sub>2</sub> fraction relatively small in normal ambient air. The same assumption has been applied to the formation of lithium hydride (Li + 1/2 H<sub>2</sub> → LiH), product of the secondary reaction between lithium and hydrogen (this latter generated from the lithium-water interaction).

## 3. CIEMAT experimental facility LiFIRE

### 3.1. DONES fire protection requirements and objectives of the LiFIRE activities

The main scope of the LiFIRE facility is to develop a set of R&D activities to support, with experimental data, the DONES safety analysis on the fire risk in the occurrence of a lithium leakage. Overall, the Defense in Depth (DiD) principle, based on prevention, detection and mitigation measures, is applied for DONES safety [5]. In particular, the outcomes from the LiFIRE experimental campaign should justify the set of preliminary fire protection requirements, presently assumed in the DONES WPENS project and collected in Table 3, for its design.

The objective of requirement #1 is to avoid or limit the occurrence of a lithium fire by preventing the exothermic reactions of the leaked lithium with air and vapor. More specifically, adequate inert conditions should be guaranteed inside the DONES rooms that contain liquid lithium (e.g., Test Cell, Lithium Trap Cell, Lithium Loop Cell) in order to limit the concentrations of nitrogen, oxygen and water vapor of the room atmosphere.

The objectives of requirement #2 are to limit the spreading of lithium leakages and to confine them to some extent. The confinement

**Table 3**  
Preliminary fire protection requirements for DONES facility.

Requirement	Safety function	Criteria	Level of the criteria	Note
1	To prevent the lithium reactions with air, water (and concrete)	Amounts of N, O and water vapor inside the cell/glove boxes Relative humidity	< 5 ppm < 2% of relative humidity at 21 °C	To be confirmed during the project
2	To prevent the spreading of the lithium leakage and receiving the fire spill	Maximum confining surface area	< 5 m <sup>2</sup>	To be confirmed during the project
3	To mitigate the lithium fire	% of Oxygen by local injection of inert gas layer of LiSO <sub>4</sub>	< 4%	To be confirmed during the project

should avoid fire damages to equipment and propagation to close materials and areas. However, promoting a large surface can be beneficial to quickly obtain lithium solidification and to avoid ignition. It is expected to find a balance between both contradictory intentions and to revise the figure provided in [Table 3](#), now established in a moderate value.

The objective of requirement #3 is to mitigate the lithium fire using fire extinguishing techniques appropriate for lithium fires (e.g., copper powder, graphite-based compounds) and by limiting the oxygen concentration in the room atmosphere with local injections of inert gas (i.e. gas flooding).

In this context, main standards concerning fire protection, like the International Fire Code (IFC) and the National Fire Protection Association (NFPA), will be reviewed for application to the DONES engineering design and for the orientation of the LiFIRE experiments in order to reduce uncertainties regarding the levels of criteria to be adopted for DONES requirements.

The main objectives pursued by the LiFIRE experimental activities are the following:

1. To reduce the uncertainty concerning specific parameters, including the ignition temperature and the maximum combustion temperature of lithium under selected conditions of atmosphere composition and humidity relevant for DONES applications (e.g., minimum oxygen concentration in an inert atmosphere able to trigger the metal ignition);
2. To demonstrate the effectiveness of gas inertization in delaying or completely avoiding the lithium ignition and in reducing the reaction rate of lithium combustion;

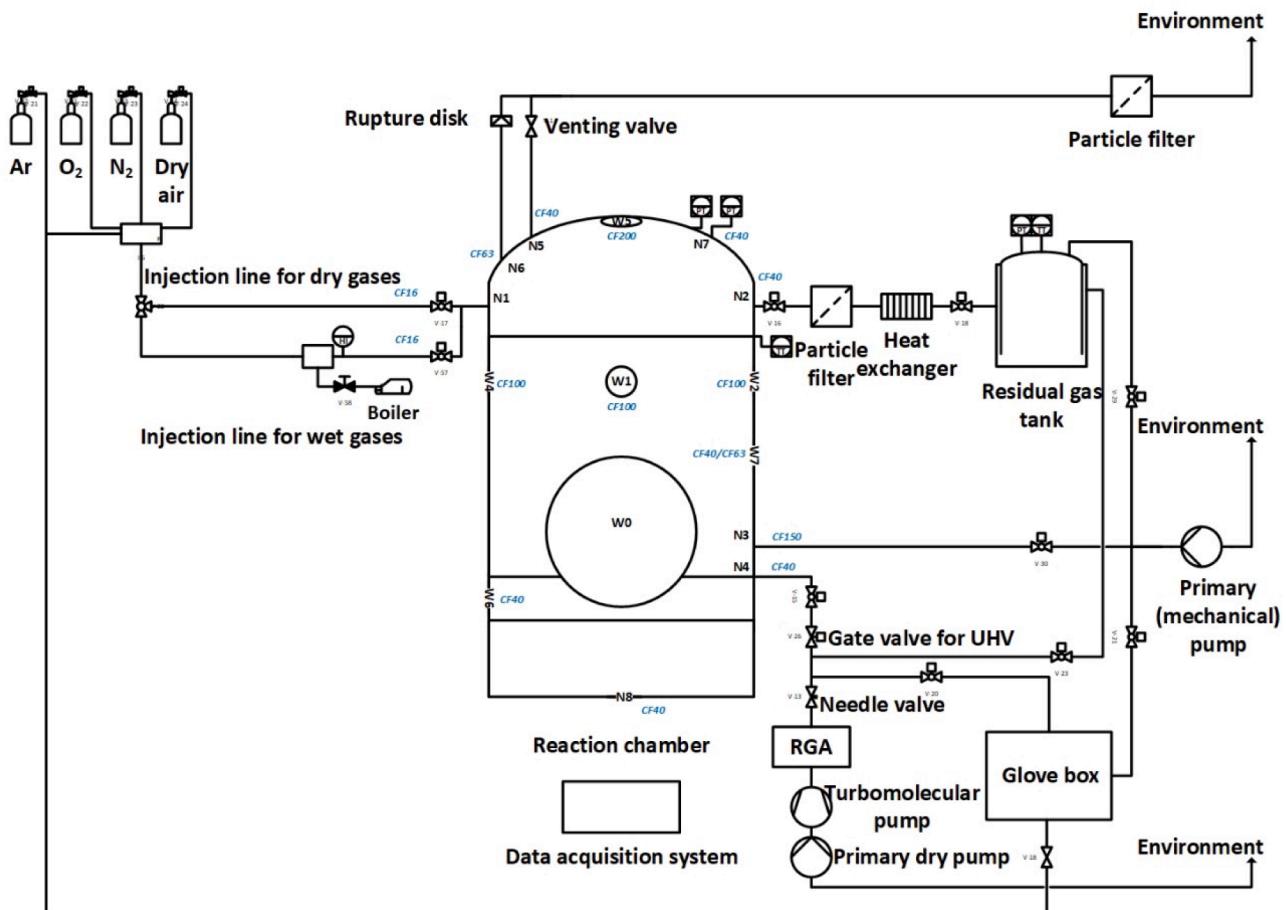
3. To monitor lithium fire consequences such as reaction rate, maximum temperatures and pressures achievable in a closed environment, generation of aerosols and solid residues from the metal combustion.

The same facility can be exploited in the future to explore different aspects directly related to lithium ignition with possible applications to experimental and irradiation facilities like DONES. Regarding the future exploratory activities for the LiFIRE facility, the following secondary objectives are preliminarily selected:

- To explore ignition conditions specifically during lithium recovery actions (e.g., chemical solvents, mechanical/thermal actions);
- To investigate the ignition behavior of lithium with surrounding materials such as heat insulators;
- To investigate the durability and compatibility of selected materials (e.g., stainless steels) with ignited lithium;
- To explore the release of carried surrogate nuclides, like stable hydrogen and beryllium (i.e., lithium hydride, beryllium nitride);
- To explore lithium ignition conditions in case of sparks;
- To assess the reliability of lithium fire detection devices (e.g., heat detectors, ionization/photoelectric detectors);
- To evaluate the efficiency and durability of aerosol retention technologies (e.g. HEPA filters, scrubbers).

### 3.2. Preliminary design of the LiFIRE facility

A preliminary process diagram of the full experimental facility has been developed and it is presented in [Fig. 1](#). Six main subsystems can be identified from the diagram:



**Fig. 1.** Preliminary process diagram of the LiFIRE facility.

Reaction chamber. Made of stainless steel, this chamber is expected to be customized with several windows (W0-W7), feedthroughs (N1-N8) dedicated to diagnostics (e.g., temperature sensors, pressure gauges, pyrometer), instrumentation (e.g., thermocouples) and other equipment (e.g., manipulators, gas nozzles, electrical power feedthroughs for heaters). For the preparation and transfer of the lithium samples inside the chamber, two solutions are currently under discussion: a separated glove box or a pre-chamber integrated to the main chamber. The chosen solution should prevent any contamination or oxidation of the metal sample prior to the execution of the experiment inside the main reaction chamber.

Gas injection subsystem. Since it is fundamental to control the moisture of the reactant atmosphere, two independent injection lines for wet and dry gases are considered. This solution allows the technician to perform experiments with dry gas mixtures avoiding potential water contamination.

Gas extraction subsystem. The gas extraction line will be equipped with a particle filter for aerosols retention, a heat exchanger for gas cooling and a residual gas tank for gas collection. A dedicated valve is also implemented for venting the chamber atmosphere before continuing with the next experiment.

Vacuum subsystem. Since proper vacuum conditions are needed to provide a sufficient control of the relative humidity inside the reaction chamber, a suitable primary dry and oil-free pump will be chosen. Measurements of the gas composition inside the chamber will be done by means of a Faraday-type RGA integrated with a primary dry pump and a turbomolecular pump.

Safety subsystem. A rupture disk connected to the reaction chamber is considered in order to mitigate overpressure events which are very unlikely scenarios. Oxygen sensors with alarms will be also installed in proper locations inside the facility room to prevent the risk of anoxia due to oxygen displacement.

Data acquisition subsystem. Dedicated data acquisition cards will be employed to record main experimental parameters of interest (e.g., ignition temperature, maximum combustion temperature).

A preliminary list of design and functional requirements relevant for the development of the final design of the LiFIRE reaction chamber is outlined. Some of these requirements, collected in Table 4, are being labelled as “secondary” since they could be modified having more flexibility than those identified as “main” requirements with small margin for possible future design modifications.

### 3.3. LiFIRE experimental campaign

Two phases have been initially identified for the experimental campaign to be carried out in the LiFIRE facility:

A Phase 1 (training phase), characterized by small-scale experiments with ignited lithium. This phase aims at gaining a basic knowledge and

**Table 4**  
Preliminary list of design and functional requirements for the LiFIRE reaction chamber.

Requirement	Value	Importance
Operating fluids	Ar, N <sub>2</sub> , O <sub>2</sub> , dry air, H <sub>2</sub> , H <sub>2</sub> O (vapor), NH <sub>3</sub> (vapor)	Main
Operational pressure range of chamber atmosphere	0.1–4000 mbar	Main
Operational temperature range of chamber atmosphere	25–600 °C	Main
Maximum design temperature of the chamber walls	200 °C	Main
Chamber type	Cylindrical with flat base and upper concave head	Main
Maximum total volume	2 m <sup>3</sup>	Secondary
Maximum outer diameter	1200 mm	Secondary
Position	Vertical	Main
Wall thickness	5–10 mm	Secondary

collecting first experiences on the main aspects of lithium ignition by exploiting limited amounts of lithium up to a few grams. Also, these first experiments can provide initial results, which can be compared to the data obtained from literature, and they can be conducted relatively quickly with foreseen limited resources.

A Phase 2, devoted to medium-scale experiments with ignited lithium. In this phase, the main objectives of the experimental activities on lithium ignition are pursued. It is foreseen to use a maximum amount of 500 g of lithium. These experiments are expected to better depict how lithium leakages behave in a closed room housing a fraction of the DONES lithium loop, and to identify the main macroscopic phenomena involved in lithium ignition.

A preliminary description of the experimental procedure has been outlined as in the following main steps:

1. Gas purging and argon filling cycles for the atmospheres of the reaction chamber, glove box/pre-chamber and residual gas tank;
2. Switching-on of the vacuum subsystem serving the reaction chamber;
3. Preparation of the solid lithium sample inside the metal crucible under controlled atmosphere composition and humidity (glove box/pre-chamber filled with argon gas to prevent contamination/oxidation of the lithium sample);
4. Transferring of the crucible with the solid lithium sample from the glove box/pre-chamber to the main reaction chamber;
5. Installation and positioning of the thermocouples inside the chamber;
6. Heating of the lithium sample by electrical heaters;
7. Injection of the specific gas mixture into the reaction chamber;
8. Gas venting and argon filling cycles for the reaction chamber and residual gas tank;
9. Cleaning process of the internal surface of the reaction chamber walls by manual action or by means of an automatic water sprinkler system and successive gas purging cycle.

### 4. Conclusions

Lithium is a highly reactive and potentially flammable alkali metal. It can easily produce exothermic reactions with atmospheric gases, water and many others materials including concrete. In the last decades, the burning behavior of alkali metals has been widely studied and mainly oriented to the research and development of nuclear facilities (e.g., sodium fast reactors) and of new technologies using metals as energy vectors (e.g., aerospace applications). Nevertheless, some aspects on the phenomenology related to metals combustion still require to be further investigated. Indeed, discrepancies regarding certain parameters and properties of metals (e.g., ignition temperature) can be noted from literature reviews.

A safe handling of alkali metals should be guaranteed and demonstrated in the case of facilities using large quantities of lithium, especially in the event of accidental spills. In this context, the LiFIRE facility, being developed at CIEMAT, aims at providing experimental evidences to support the fire protection requirements applied to the DONES facility and to minimize the risk of fires under accident conditions. The main objectives of the LiFIRE experimental activities are to reduce the uncertainty of specific parameters regarding lithium combustion, to demonstrate the effective use of an inert gas in limiting or avoiding a lithium fire and to monitor its consequences. It is foreseen to study and characterize the main phenomena governing the lithium ignition under selected conditions of atmosphere composition and humidity relevant for DONES applications.

A preliminary process diagram of the LiFIRE facility has been developed and its main subsystems have been identified based on the layout of similar past experimental facilities. A list of main design and functional requirements applicable to the reaction chamber, where the lithium experiments will be carried out, has been outlined.

The experimental campaign has been divided into a first training phase aimed at collecting first experiences using small quantities of lithium, and a second phase devoted to the study of the main macroscopic phenomena involved during lithium ignition.

#### CRediT authorship contribution statement

**Gianluca D'Ovidio:** Investigation, Conceptualization, Writing – original draft, Writing – review & editing, Visualization. **Francisco Martín-Fuertes:** Investigation, Conceptualization, Writing – review & editing. **Daniel Alegre:** Investigation, Conceptualization, Writing – review & editing. **Juan Carlos Marugán:** Investigation, Writing – review & editing. **Adrián Pitigoi:** Investigation, Writing – review & editing. **Javier Sierra:** Writing – review & editing, Supervision, Funding acquisition. **Joaquín Molla:** Writing – review & editing, Supervision, Funding acquisition.

#### 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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