F. Chalghoum, D. Trache, F. Maggi, M. Benziane
Effect of Complex Metal Hydrides on the Elimination of Hydrochloric Acid Exhaust Products from High-Performance Composite Solid Propellants: a Theoretical Analysis
Propellants, Explosives, Pyrotechnics, Vol. 45, N. 8, 2020, p. 1204-1215
doi:10.1002/prep.201900408

Effect of complex metal hydrides on the elimination of hydrochloric acid exhaust products from high-performance composite solid propellants: A theoretical analysis

Fateh Chalghoum[1,2], *Djalal Trache*[*,1], *Filippo Maggi*[3], *Mokhtar Benziane*[2]

[1]UER Procédés Energétiques, Ecole Militaire Polytechnique, BP 17, 16046, Bordj-el-Bahri, Algiers, Algeria
[2]Ecole Supérieure du Matériel ESM, BP 188, Beau-Lieu, Algiers, Algeria
[3]Department of Aerospace Science and Technology, Politecnico di Milano, 34 Via La Masa, 20156 Milan, Italy

[*]Corresponding author
E-mail Address: djalaltrache@gmail.com
ORCID: 0000-0002-3004-9855

Abstract

Ammonium perchlorate (AP)-based solid rocket propellants generate hydrochloric acid (HCl) as an exhaust product during combustion. This latter displays numerous environmental problems such as the depletion of the ozone layer and the increase of the concentration of acid rains. This paper offers a theoretical analysis concerning the employment of metal hydrides as efficient additives to mitigate some of the negative effects of HCl on the environment during the combustion of AP-based composite propellants. Nine complex metal hydrides, expected to generate desirable performance gains, are selected to assess their scavenging effect on the HCl during propellant combustion. Based on NASA Lewis Code, Chemical Equilibrium with Application (CEA), comparative analysis of the theoretical performance of specific impulse, adiabatic flame temperatures, condensed combustion products as well as the exhaust gaseous species has been carried out. This study reveals that complex metal hydrides-based propellants exhibited better performance than those containing simple metal hydrides, showing a synergetic effect of high specific impulse and low environmental impact. It is consequently anticipated that a good choice of metal hydride can provide clean/green propellant formulations that can satisfy the current environmental requirements with better performance than current aluminum propellants.

Keywords: Solid propellant; green propellant; metal hydride; hydrochloric acid; environmental impact; theoretical performance

1. Introduction

Composite solid propellants (CSPs) are widely employed in space exploration and defense technology for several decades [1-4]. They are designed to accelerate projectiles, rockets, missiles, space launchers, or airplane ejection seats by producing propulsive force. Owing to their promising features such as acceptable cost, good mechanical and burning properties, simplicity, reliability, as well as ease of processability and storability, the most mature propellant formulation contains ammonium perchlorate (AP) as oxidizer, hydroxyl-terminated polybutadiene (HTPB) as binder and aluminum (Al) as fuel [5]. AP-based composite solid propellants negatively interact with the atmosphere by releasing hydrochloric acid (HCl) as one of the main exhaust products. Thermodynamic computations predict that a typical composition used in Ariane V boosters and composed in mass fractions by 68 % of AP, 18 % of Al, and 14 % of elastomeric binder produces about 21 % of hydrochloric acid. Also Space Shuttle propellant expels the same high level of HCl (21 %) [6], polluting the stratosphere as well as the land and water sources. The launch of six Titan class vehicles can cause the ozone depletion in addition to a dramatic increase of the stratospheric acidic rain [7]. Further potential issue in military applications is that HCl gas forms nucleation sites for aerosolized water products, which generate a secondary smoke from the exhaust plume that may be either visible or detected with radar [8]. Therefore, the next generation of solid propellants have to take into account the environmental considerations, while at the same time maintaining high performance.

The first approach widely explored is dedicated to the substitution of AP by other energetic oxidizers. Trache et al. have recently reviewed the potential candidates that can be used as replacement of AP [2]. Unfortunately, for practical applications there are currently no fielded chlorine-free solid oxidizers that present similar or better performance than AP. The second alternative approach that seems to be efficient to mitigate the environmental negative impact of AP-based composite propellants concerns the reduction, elimination or scavenging of HCl during combustion. One possibility is to incorporate alkali metals [9]. Klapötke has mentioned that the addition of NaNO3 allows to transform the gaseous chlorine to NaCl [10]. Doll and Lund revealed that the incorporation of Mg allowed the preparation of low-acid propellant that represents a major step forward in the realm of environmentally benign solid propulsion technology [6]. In this respect, extensive experimental work was presented by D'Andrea and co-authors [11]. However, these approaches may negatively influence the safety requirements or decreases the performance. Thus, other additives or ingredients have to be developed and introduced into propellant formulations, exhibiting high performance and environmentally benign combustion products. It is important to note that not only the theoretical energetic performance is considered for solid propellant selection, other characteristics may have a great importance such as burning rate, mechanical behavior, smokeless consideration, safety and vulnerability, aging proprieties and production cost [12, 13]. Thus, suitable choice has to take into account the various above mentioned parameters.

Simple and complex hydrides have been revealed for several years as interesting fuels to substitute Al in composite propellants [14-20]. They can improve the performance and decrease the agglomeration process during combustion. Recently, Maggi et al. have mentioned that metal hydrides can also neutralize and decrease the HCl content released during the combustion of AP-based propellants [13]. As mentioned above, intensive research works have been dedicated to the assessment of the effect of various metal hydrides on the performance of composite propellants without addressing a deep investigation on their effect on the scavenging of HCl exhaust products. Therefore, there is a need to understand and evaluate the effect of such fuels on the scavenging and neutralization of HCl released from propellant combustion. In the present work, based on theoretical approach, we thoroughly examined the effect of some prominent complex metal hydrides incorporated in AP-based composite solid propellants on the performance and elimination of hydrochloric acid from the exhaust gaseous products. A comprehensive comparison of theoretical specific impulse, adiabatic flame temperatures, condensed combustion products as well as the exhaust gaseous species, especially HCl, has be undertaken.

2. Theoretical background and computational details

2.1. Hydrochloric acid elimination from CSPs

Typically, two approaches are widely pursued to decrease the amount of HCl in AP-composite solid propellants: (1) the employment of formulations without or with less content of chlorine, and (2) neutralization of HCl in the combustion plume, its scavenging or conversion. The second methodology can be reached through the incorporation of various additives. Some alkali metals such as Li, Na and K as chlorine ion scavengers have been tested and they exhibited the ability to reduce the HCl amount in composite solid propellant exhaust products [9, 12]. However, these latter are highly reactive and are consequently not directly used as neat elemental alkali metals. Furthermore, compared to Al fuel, Mg or other alkali metals incorporation to CSP can negatively affect their performance in terms of specific impulse or density. Metal hydrides have received huge attention and have been revealed to be promising metal-based fuels for CSPs. They provide better HCl scavenging characteristics, high performance as well as low gaseous molecular mass owing to hydrogen release during combustion process [9, 21, 22]. This latter class of materials is the focus of the remaining part of the paper.

The scavenging effect of some metal fuels, which are incorporated to composite propellant formulations in the form of complex hydrides, can be determined through the evaluation of the high performance halide scavenger (HPHS) parameter [9] determined by equation (1) and proposed by Brandon C. Terry *et al.* [9, 23].

$$HPHS = \left(\frac{I_{sp}}{I_{sp,max}}\right).[100 - (\%Cl \rightarrow HCl)] \qquad (1)$$

In the formula I_{sp} is the specific impulse delivered by the mixture ingredient ratios constituting the given propellant formulation, $I_{sp,max}$ stands for the maximum specific impulse achieved when varying the fractions and keeping the ingredient types of the given propellant formulation. An HPHS value of 100 % means that complete HCl reduction is occurring, while maintaining the same specific impulse. The following relations display the methodology to determine HPHS based on equation 1.

$$(\%Cl \rightarrow HCl) = 100\frac{n(Cl \rightarrow HCl)}{n_T(Cl)} \tag{2}$$

$$n(Cl \rightarrow HCl) = n_T . \chi(HCl) \tag{3}$$

$$n_T(Cl) = n_T . \sum i . \chi\,(MCl_i) \tag{4}$$

$$(\%Cl \rightarrow HCl) = \frac{n(Cl \rightarrow HCl)}{n_T(Cl)} = \frac{n_T . \chi(HCl)}{n_T . \sum i\,.\,\chi\,(MCl_i)} = \frac{\chi(HCl)}{\sum i\,.\,\chi\,(MCl_i)} \tag{5}$$

$n(Cl \rightarrow HCl)$: Moles number of the chlorine atoms, which formed the hydrochloric acid;

$n_T(Cl)$: Total moles number of chlorine atoms;

n_T: Total moles number of species resulting from propellant combustion;

$\chi(HCl)$: Molar fraction of the hydrochloric acid;

$\chi(MCl_i)$: Molar fraction of the molecule MCl_i, which contains *i* atoms of chlorine in its molecular structure.

All moles number and molar fractions of the mentioned species have been calculated at the nozzle exit section.

2.2. Complex metal hydrides for CSPs

Solid hydrogen storage materials, such as simple metal hydrides (AlH_3, ZrH_2, BeH_2, MgH_2), nitrides (Li-nitrides, metal amine complexes), and complex metal hydrides (alanates, borohydrides, magnesium-based hydrides) are very useful for a wide range of applications encompassing hydrogen generation, hydrogen storage and reducing agents [24, 25]. These materials have been proposed as prominent candidates in energetic materials and pyrotechnics, owing to their relatively high hydrogen content [13, 17]. The incorporation of hydrogen in propellant formulations has been revealed as an adequate solution to improve the specific impulse and the heat of combustion, since hydrogen can enhance the combustion performance and reduces the ignition delay. It is expected that the dehydrogenation of hydrides at temperatures below typical motor flame temperatures can enhance specific impulse. The base metal left behind reacts as well, providing extra reaction enthalpy [18, 26-28].

Various simple metal hydrides (SMH) such as AlH_3, TiH_2, BeH_2, MgH_2 and ZrH_2 have been tested as fuels of composite solid propellants [18, 21, 22, 29]. They seemed to be promising alternatives to common metal fuels, since they are found to be capable of enhancing performance through the decrease of the gaseous molecular mass due to hydrogen as well as the reduction of the two-phase flow losses. However, these simple metal hydrides, except for ZrH_2, present low density compared to that of aluminum, which causes the decrease of the volumetric loading [29]. In addition, they are very difficult to handle safely, are very sensitive to moisture, and can dehydrogenate and oxidize prematurely [30]. Compared to SMH, complex metal hydrides (CMH) usually possess higher hydrogen storage capacity such as $LiBH_4$ (18.5 %), $LiAlH_4$ (10.5 %) and $LiMgAlH_6$ (9.4 %). These compounds also exhibit long-term stability and have been found to improve the burning performance of composite propellants as well as to shorten ignition delay, intensifying energy release [18, 26, 31, 32].

Complex metal hydrides composed of light alkali elements such Li, Na and K gained significance as hydrogen storage materials since conventional metal hydrides are mostly composed of heavy elements in the periodic table of elements [25, 33]. Complex alkali metal hydrides are expected to be potential fuels for composite solid propellants due to their synergetic effect in improving performance and scavenging hydrochloric acid [9, 18, 25, 26, 33]. They can significantly decrease the condensed phase combustion products, as their oxides, fluorides, and chlorides present low volatilization temperatures improving, at the same time, the combustion features owing to their relatively high hydrogen content. Moreover, such complex hydrides can efficiently scavenge almost all of the hydrochloric acid within propellant combustion products thanks to their halophilic nature. In this respect, Li-based complex hydrides remain one of the most prominent class to be used as solid propellant fuels [34]. Furthermore, the introduction of oxophilic materials such as Al, B and Mg can improve the stability of the Li-based hydrides, increase the scavenging effect and enhance the specific impulse of composite solid propellants [6, 9, 18, 25, 26, 33], as it will be discussed below.

2.3. Performance of composite solid propellants

Theoretically, it is clear that by increasing the ratio of adiabatic flame temperature to combustion products molar mass (T_c/M_m), the specific impulse (I_{sp}) can achieve higher values. Volumetric specific impulse, given by $I_{sp,v} = \rho_{\mathrm{p}}.I_{sp}$, is commonly considered more effective for evaluating solid propellant performance. To design high energetic and efficient propellants, one should select propellant ingredients that provide higher combustion flame temperatures with low average molecular weight exhaust products [35], within the constraint of reasonable thermal wall fluxes to reduce the inert mass of thermal protections [36]. Based on (1) chemical composition of the propellant formulation, (2) different equilibrium reactions, and (3) thermodynamic calculations of decomposition reactions, some thermochemical codes are usually applied to compute the theoretical specific impulse delivered by propellant combustion into ideal rocket motor [12, 37]. Typically, such theoretical I_{sp} is not totally reached in a real systems. It has been estimated that about 10 % of losses should be accounted for in a standard rocket motor burning aluminized propellant because of incomplete chemical reactions, agglomeration, throat erosion phenomena, two dimensional flow at nozzle exit, and boundary layer, among others [38].

2.4. Evaluation of CSPs Performance

To study the effect of some metal complex hydrides as energetic fuel additives on the performance of AP/HTPB composite solid propellants, the NASA CEA thermochemical computer program was applied [39, 40]. A number of assumptions are taken into account to compute the main energetic parameters of composite solid propellants. The fundamental ones used in the present work are: (1) complete and adiabatic combustion in solid propellant motor chamber, (2) one-dimensional and isentropic expansion gaseous flow, (3) chemical equilibrium throughout expansion, and (4) absence of two-phase flow losses [12, 40]. Based on an iterative procedure for minimization of Gibbs free energy, CEA calculates the thermochemical equilibrium compositions of the combustion products at different nozzle sections [40].

In the present work the combustion and the exit pressures of 7 MPa and 0.1 MPa are taken, respectively, the supersonic section ratio is considered to be A_e/A_t=10, whereas the initial temperature is 298 K. The molecular structure of HTPB binder is $C_{7.075}H_{10.65}O_{0.223}N_{0.063}$ with standard formation enthalpy ΔH_f=-58 kJ/mol [13, 41].

In the present study, various complex metal hydrides have been tested as fuels of CSPs. Some of CMHs such as $NaAlH_4$, Mg_2NiH_5, Mg_2CoH_5, Li_2NH and $LiNH_2$ did not show any improvement on the specific impulse of AP/HTPB based propellants. Thus, they have been excluded from the investigation. Only good candidates of CMHs, which provide acceptable theoretical specific impulse, have been maintained for the next parts of the study.

Table 1. Potential complex metal hydrides as energetic additives for CSPs.

Complex hydride	ΔH_f [kJ/mol]	Density [g/cm^3]	H_2 density [Mass %]	Ref
Li_4FeH_6	-379.0	/	6.7	[32, 42]
$LiAlH_4$	-113.4	0.92	10.6	[13, 43]
Mg_2FeH_6	-232.2	2.74	5.5	[32, 42, 44]
$Mg(AlH_4)_2$	-82.8	2.24	9.3	[45-47]
Na_3AlH_6	-216	1.45	5.5	[48, 49]
$KAlH_4$	-166	/	5.7	[50, 51]
$LiMgAlH_6$	-186.4	/	9.4	[45, 52]
$LiMg(AlH_4)_3$	-166.7	1.80	9.7	[43, 45, 47]

As shown in Table 1, eight complex metal hydrides have been selected to assess their efficiency on the elimination of HCl from AP/HTPB propellants. Two reference formulations (AP/HTPB and AP/HTPB/Al) have been also considered for comparison. The optimal propellant compositions, targeting the highest specific impulse, have been determined using CEA either for formulations, which require a minimum amount of HTPB as binder (10 %) [13], named as “optimal composition”, or formulations without any constraints that provide the maximum theoretical specific impulse, named as “unconstrained optimal composition (Table 2).

Table 2. "Optimal composition" and "Unconstrained optimal composition" for AP/HTPB/additive propellants.

Additive	Optimal composition [Mass %]			$I_{sp,opt}$ [s]	Unconstrained Optimal composition [Mass %]			$I_{sp,max}$ [s]
	AP	HTPB	Additive		AP	HTPB	Additive	
Baseline	89	11	0	254.0	89	11	0	254.0
Al	69	11	20	263.4	69	11	20	263.4
Li_4FeH_6	82	10	8	259.6	83	8	9	260.4
$LiAlH_4$	60	10	30	281.7	59	0	41	288.9
Mg_2FeH_6	67	12	21	264.0	67	12	21	264.0
$Mg(AlH_4)_2$	60	10	30	278.0	60	7	33	278.4
Na_3AlH_6	85	10	5	254.6	79	7	14	255.5
$KAlH_4$	85	10	5	254.4	83	9	8	254.6
$LiMgAlH_6$	58	10	32	276.4	58	6	36	277.6
$LiMg(AlH_4)_3$	60	10	30	282.1	56	0	44	288

3. Results and discussion

3.1. Determination of the optimal composition of propellant formulations

"Constrained optimal composition" of different CSPs and their corresponding performance parameters have been computed on the basis of the highest possible specific impulse and the results shown in Tables 2 and 3, respectively. In the optimization process, a minimum binder amount of 10 % was imposed for practical feasibility. It should be mentioned that the proposed minimum binder quantity is only indicative and depends not only on the respective mass fractions but also on ingredient densities and particle size as well as mixture compatibility and pot-life. All these last aspects are not part of the present work and require dedicated studies once candidate compositions are selected. The reported performance parameters comprise optimum specific impulse ($I_{sp,opt}$), adiabatic flame temperature (T_c), combustion products molar mass (M_m), condensed combustion products (CCPs), exhaust combustion products (ECPs), and "high performance halide scavenger" (HPHS) parameter. The calculated "optimal composition" and its corresponding highest specific impulse ($I_{sp,max}$) of the different propellant formulations are also reported in Table 2, and consider a condition where minimum binder amount is not taken into consideration. These compositions may be impossible to mix and cast and represents only an ideal reference for highest attainable performance.

The analysis of the delivered theoretical specific impulse plotted in Fig. 1a highlighted an improvement of the performance for all propellants containing the selected CMHs. The highest performance values have been obtained for the propellants containing $LiMg(AlH_4)_3$, $LiAlH_4$, $Mg(AlH_4)_2$ and $LiMgAlH_6$. These ternary and quaternary CMHs include mainly lithium, magnesium and aluminum in intermetallic compound forms. In most cases, the constraint on minimum binder is enacted obtaining a discrepancy between optimal and maximum specific impulse lower than 10 s. As shown in Fig. 1b, some propellant formulations with optimal specific impulses at high metal hydride contents (≥ 30 %) can also deliver higher performance than Al-based formulation (I_{sp}=164 s) even at low CMH mass fractions (≥ 10 %), hence providing the possibility of producing desired formulations for practical feasibility.

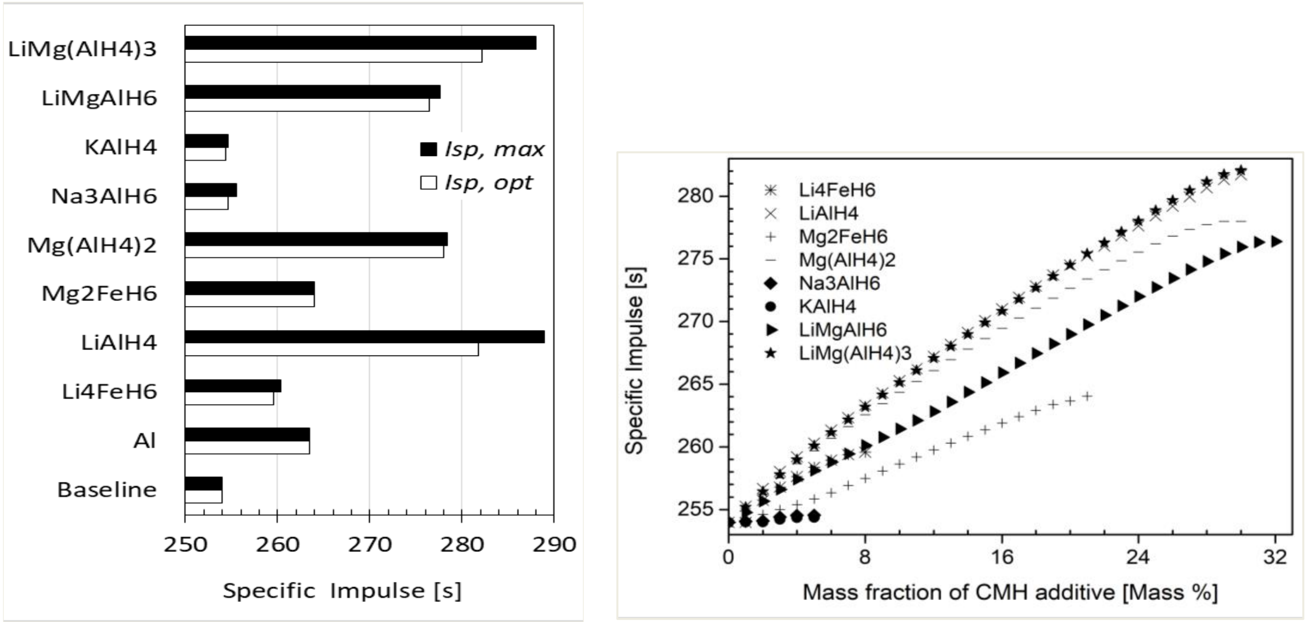


Fig. 1. (a) Maximal and optimal calculated specific impulses obtained by AP/HTPB/additive propellant; **(b)** Specific impulse evolution with respect to the additive mass fraction, until the optimal composition.

As illustrated in Fig. 2, the specific impulse values obtained when incorporating the fuel additives into the AP/HTPB formulations have been improved. The addition of 30 % of $LiMg(AlH_4)_3$ or $LiAlH_4$ to AP/HTPB propellant formulation has led to an increase in specific impulse of nearly 11 %. The theoretical maximum specific impulse presented in Table 2 has been reached with propellant formulations containing a low binder mass fraction (less than 10 %), with the exception of propellants containing, respectively, magnesium iron hydride (12 %) and aluminum (11 %). Comparing the I_{sp} values of the solid propellants containing metal hydrides with that of AP/HTPB/Al composite propellant, the CMHs group including $KAlH_4$, Na_3AlH_4 and $LiFe_4H_6$ did not provid any improvement to the propellant performance ($I_{sp} < 263$ s).

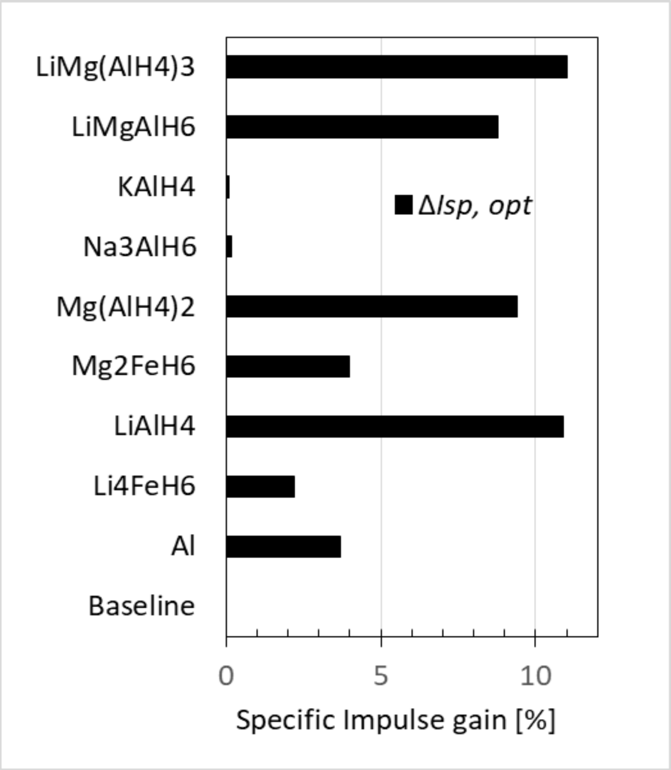


Fig. 2. Optimal specific impulse normalized to baseline formulation AP/HTPB (89/11).

3.2. Ideal combustion characteristics

The temperature of the combustion products and their average molecular weights for various propellants are presented in Fig. 3. It is observed that the combustion flame temperatures achieved using metal hydrides are lower than that of AP/HTP/Al propellant (Table 3). This may be explained by the heat loss caused by the dehydrogenation reactions and the dilution caused by unburnt H_2 [14]. The amount of hydrogen available in metal hydrides is released endothermically at low temperature and sensible enthalpy is used to increase its temperature.

Table 3. The predicted combustion characteristics and performance parameters for AP/HTPB/additive propellants (Constrained Optimal composition).

Additive	$I_{sp,opt}$ [s]	T_c [K]	M_m [g/mol]	CCPs [Mass %]	Cl → HCl [%]	HPHS [%]
Baseline	254.0	3037	26,6	0	100.0	0.0
Al	263.4	3637	30.3	35	98.,5	1.5
Li_4FeH_6	259.6	3164	26.3	0	11.2	88.6
$LiAlH_4$	281.7	2976	21.2	43	1.9	95.7
Mg_2FeH_6	264.0	3173	26.6	13	0.0	100.0
$Mg(AlH_4)_2$	278.0	3141	23.4	43	80.3	19.7
Na_3AlH_6	254.6	3092	26.9	2	79.7	20.3
$KAlH_4$	254.4	3107	27.1	3	90.1	9.9
$LiMgAlH_6$	276.4	2845	21.7	42	0.8	98.8
$LiMg(AlH_4)_3$	282.1	3120	22.5	43	49.8	49.2

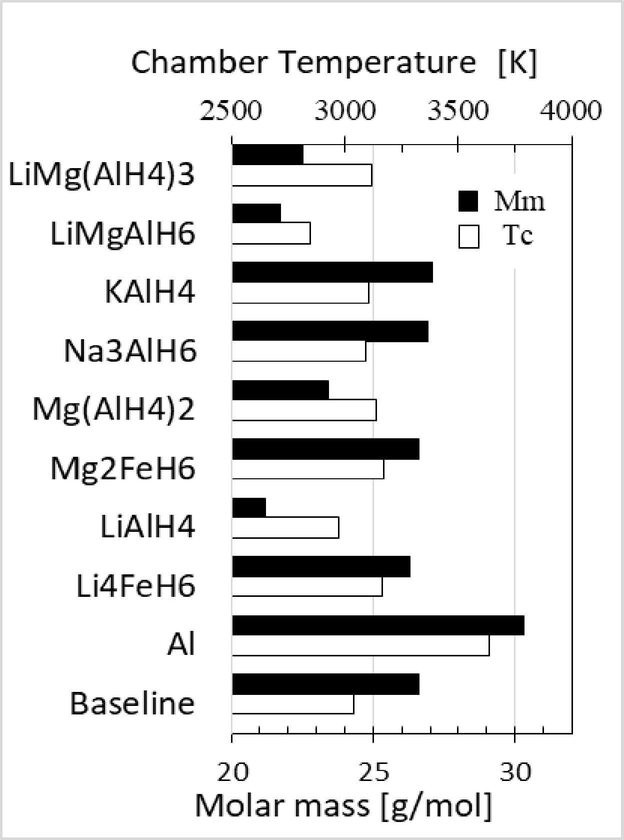


Fig. 3. Combustion characteristics prediction for additive/AP/HTPB propellant optimal compositions.

The replacement of aluminum with a metal hydride in AP/HTPB-based formulation leads to the reduction of the average molar mass of the combustion products. A decrease of more than 30 % in average molecular weight of the combustion products has been achieved by using lithium aluminum hydride instead of metallic aluminum. This is attributed to the high gravimetric hydrogen density of

CMHs, which increases the hydrogen mole fraction released into the combustion chamber. The low gravimetric density of the metal substrates contained in solid hydride fuels can also reduce the average molecular weight by forming low molar mass metal oxides [14]. Therefore, the ideal specific impulse obtained by these new CSPs is improved with respect to baseline propellants because the decrease of the combustion flame temperature can be balanced by the reduction of the average molecular weight of the combustion products, globally producing an increment of the T_c/M_m ratio.

Indicative considerations on two-phase flow expansion losses can be made by tracking the condensed combustion products exiting from the nozzle. During the combustion of the analyzed compositions, liquid or solid products can be formed essentially by the oxidation reactions of the metal substrates of complex hydride additives [13, 28, 53]. The predicted weight of condensed products given by complete combustion of 100 g of optimal composition propellants are reported in Fig. 4, where the combustion product mass fractions have been computed at nozzle throat section. The use of certain CMHs such as Na_3AlH_6, $KAlH_4$ and Li_4FeH_6 led to a significant reduction of CCPs at nozzle throat (almost 100 % CCPs reduction has been obtained by Li_4FeH_6 fuel additive) as reported in Table 3. The incorporation of 21 % of magnesium iron hydride to propellant formulation produces lower condensed species, compared to aluminized AP/HTPB propellant (more than 62 % of CCPs reduction has been achieved).

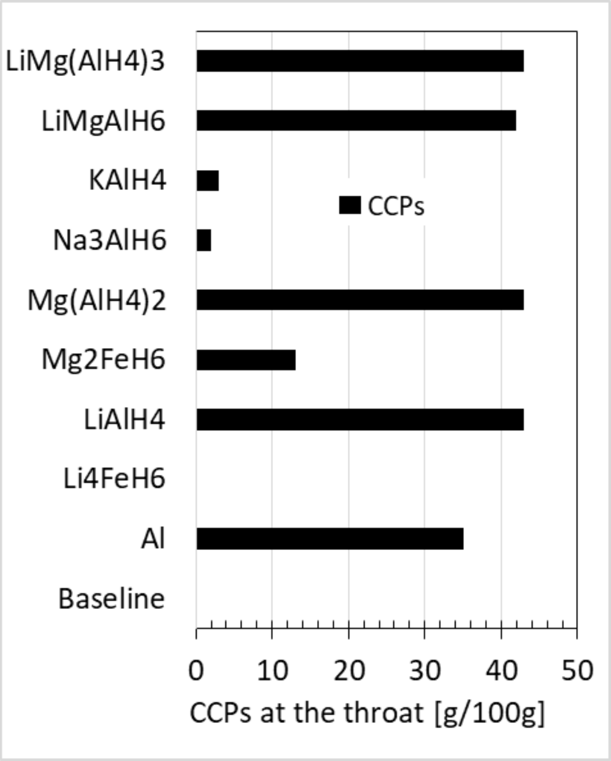


Fig. 4. Condensed combustion products for AP/HTPB/additive propellant optimal compositions at nozzle throat section

3.3. Theoretical volumetric specific impulse

Most of the metal hydrides previously tested as fuel additives in composite solid propellants presented lower density than aluminum (ρ = 2.7 g/cm^3), except for barium hydride (ρ = 4.21 g/cm^3), zirconium hydride (ρ = 5.67 g/cm^3), strontium hydride (ρ =3.26 g/cm^3) and titanium hydride (ρ = 3.9 g/cm^3) [13, 14, 54]. Therefore, the replacement of Al in AP-HTPB-based propellant formulations with a low density metal hydride decreases the composition theoretical density [13]. In the present paper, magnesium iron hexahydride (Mg_2FeH_6) has the highest value density (Table 1). This latter complex transition-metal hydride, recently synthesized in its pure state [44], has attracted great attention due to its high stability compared with MgH_2 and its highest volumetric hydrogen density (150 kg/m^3), in addition to the large abundance and low cost of iron and magnesium [55-59]. Table 4 displays the calculated $I_{sp,v}$ delivered by three AP/HTPB propellants at optimal compositions. The obtained results highlighted that the incorporation Mg_2FeH_6 increases of almost 8 % the volumetric specific impulse of AP/HTPB propellant formulation thanks to both higher gravimetric specific impulse and density. When compared to optimal aluminized composition, this one has the benefit to reduce of about 2/3 to 13 % the CCPs and completely remove the hydrochloric acid from the exhaust, maintaining similar performance and density.

Table 4. Volumetric specific impulse of AP/HTPB propellants containing Al and Mg_2FeH_6 as energetic additives (Constrained Optimal composition).

Samples	Optimal composition	I_{sp} [s]	ρ_p [kg/m^3]	$I_{sp,v}$ [s.kg.m^{-3}]	$I_{sp,v}$ improvement
AP/HTPB	89/11	254.0	1736	4.41×10^5	
AP/HTPB/Al	69/11/20	263.4	1827	4.81×10^5	9 %
AP/HTPB/Mg_2FeH_6	67/12/21	264.0	1816	4.79×10^5	8.6 %

3.4. Analysis of hydrochloric acid elimination from CSPs

The effect of inorganic combustible additives on molar fraction of the gaseous species has been analyzed in Fig. 5

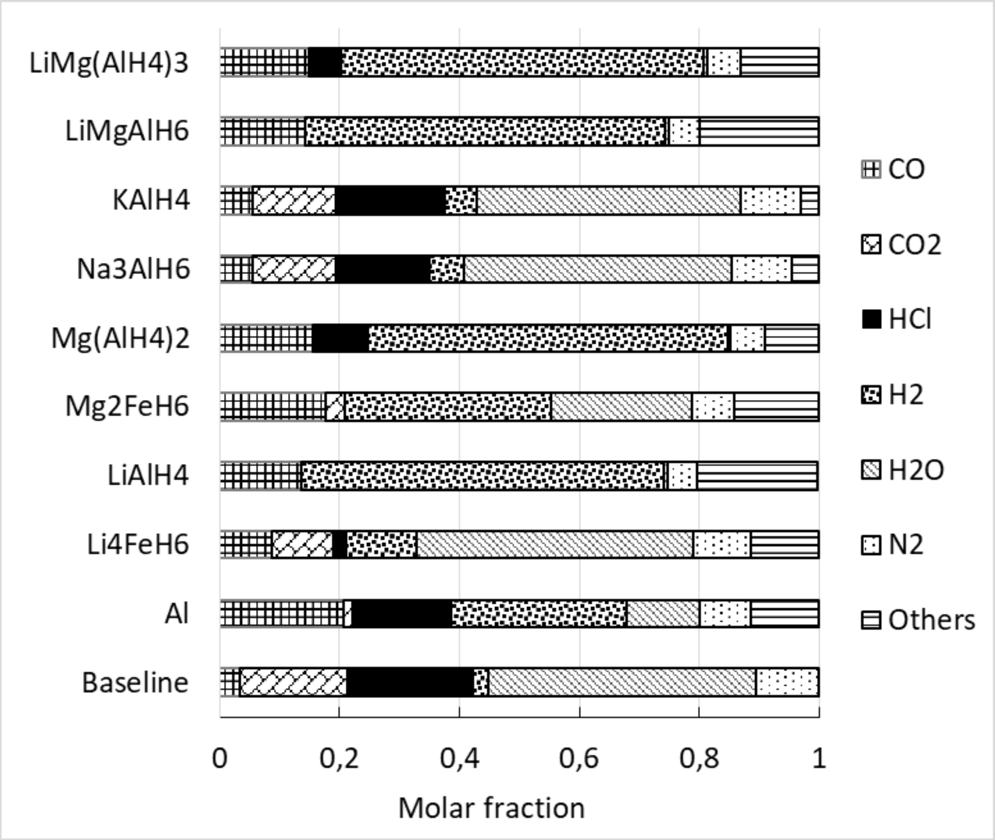


Fig. 5. Exhausts products for AP/HTPB/additive propellant optimal compositions.

The exhaust combustion products of AP/HTPB baseline propellant contain only gaseous molecules, corresponding to H_2O, CO_2, HCl, N_2, CO and H_2. Complex hydrides generate high hydrogen concentration in most of the cases, with the exception of compositions based on $KAlH_4$, Na_3AlH_6, and Li_4FeH_6, where water is predominant. The high amount of the exhausted hydrochloric acid has been significantly reduced by the addition of some inorganic fuels such as $LiAlH_4$, Mg_2FeH_6, and $LiMgAlH_6$. Based on the HPHS parameter defined in equation 1, the ability to remove the evolved hydrochloric acid in combustion products has been examined. The values of this performance criterion obtained for various propellant (optimal compositions) are plotted in Fig. 6. It was shown that Mg_2FeH_6 exhibited the highest HPHS value (HPHS > 99.9 %), which means that almost total hydrochloric acid elimination has been obtained by the AP/HTPB propellant formulation containing 21 % mass fraction of magnesium iron hydride. Furthermore, such formulation presented higher value of specific impulse with respect to that of AP/HTPB/Al. Thus, Mg_2FeH_6 could be considered as a prominent fuel candidate for green composite solid propellants, if other requirements such as compatibility and stability, among others, are positively fulfilled.

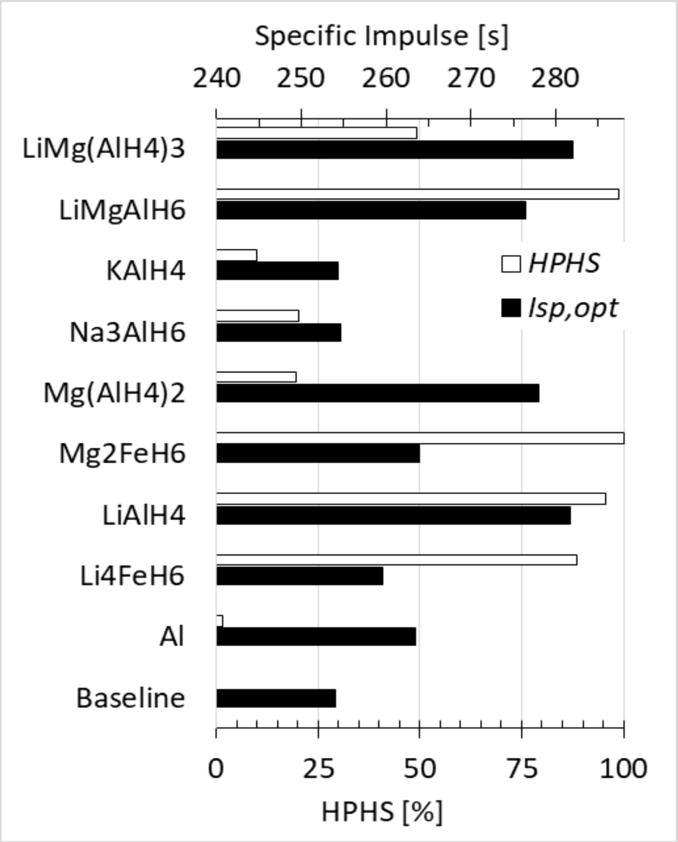


Fig. 6. HPHS parameter values for the / AP/HTPB/additive propellant optimal compositions.

On the other hand, it is well known that HCl molecules produced from complete decomposition of AP at high temperature have a tendency to react with metal hydride particles, which contained some alkaline atoms such as Li, K, and Na [9, 13, 41]. However, as shown in Fig. 7, in contrast to what is expected, lower HPHS values have been obtained when sodium and potassium aluminum hydrides have been employed (HPHS = 20.3 % and 9.9 % respectively). This result may be attributed to the low mass fractions of these incorporated complex hydrides in CSPs at optimal compositions. Thus, the amount of potassium and of sodium are insufficient to convert all the available chlorine in chlorine alkali metal compounds.

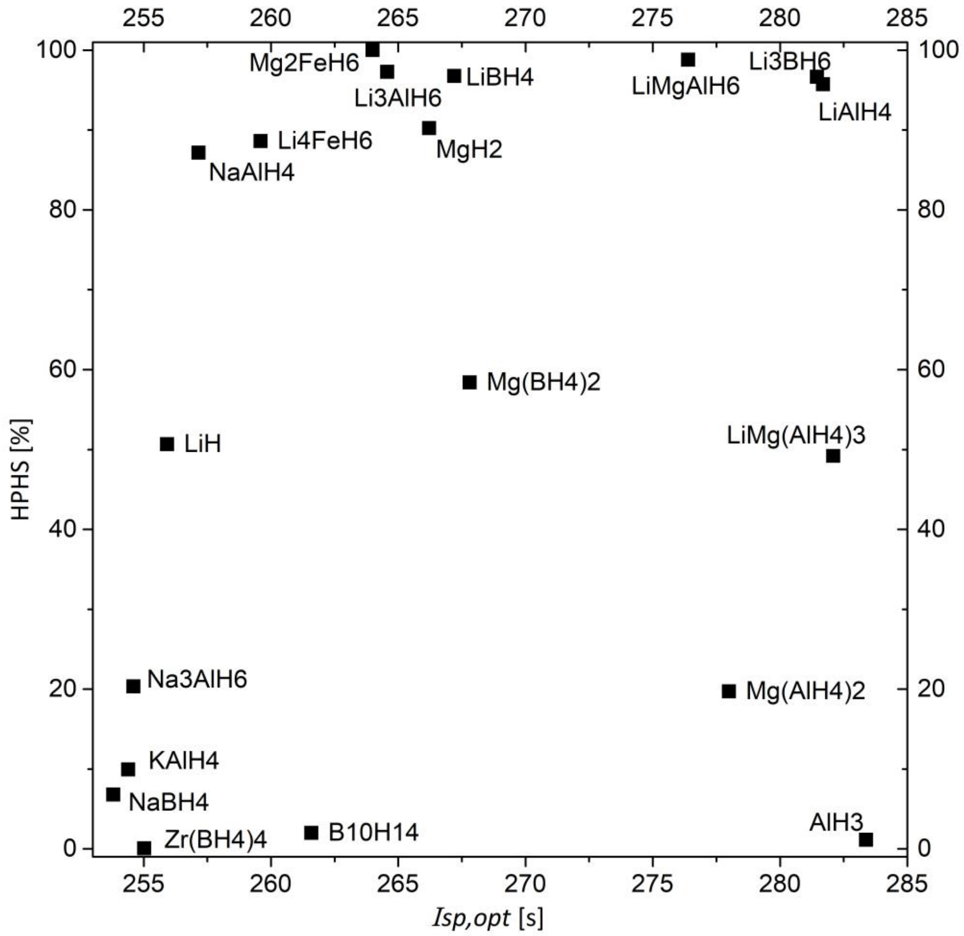


Fig. 7: Specific impulse and “High Performance Halide Scavenger” parameter of some metal hydrides

To better understand the performance and halide scavenger effect of the investigated complex metal hydrides a plot exhibiting the role of nineteen metal hydrides (simples and complexes) on the performance and environmental impact based on their coordinates (I_{sp}, HPHS) is reported in Fig. 7. Data suggest that Li-CMHs containing oxophilic materials such as B, Al and Mg, provide highest synergetic effect with higher I_{sp} (> 276 s) and low environmental impact (HPHS > 95.7 %). This category includes Li_3BH_6, $LiAlH_4$ and $LiMgAlH_6$. The simple metal hydrides however showed low synergetic effect (HPHS < 1.2 % for AlH_3 and I_{sp} < 256 s for LiH,).

Typically, the chlorine atoms available in AP can be principally converted during combustion process either to chloride hydrogen gas or chloride metal compounds. Fig. 8 showed the chlorine conversion during the complete combustion of propellants containing the most interesting complex metal hydrides that delivered the highest HPHS values. For instance, the addition of 21 % mass fraction of magnesium iron hydride to AP/HTPB propellant formulation led almost to the total conversion of chlorine amount to iron (III) chloride.

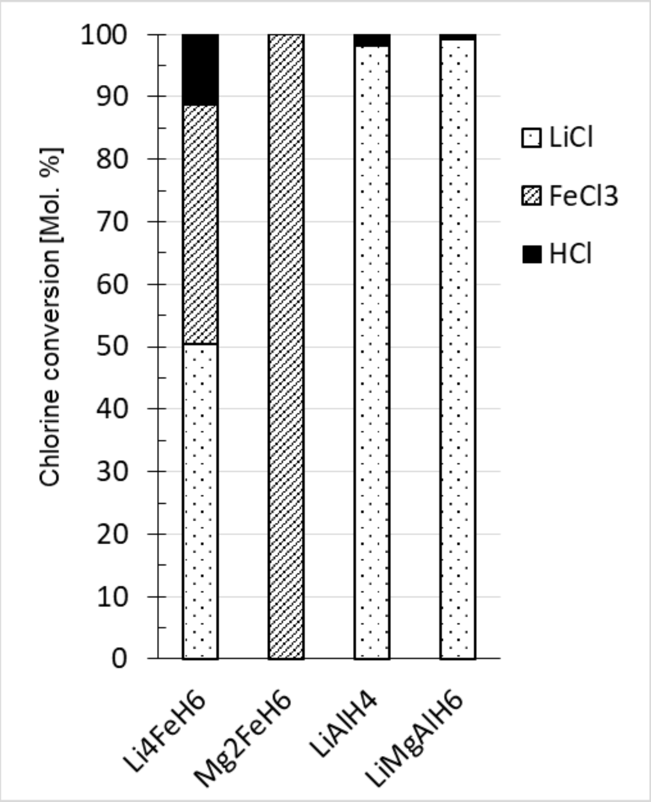


Fig. 8. Chlorine conversion at optimal compositions for "high performance halide scavenger" propellants.

In the case of the incorporation of $LiAlH_4$ or $LiMgAlH_6$, the halide scavenger effect was attributed to lithium that ensures the conversion of 98 % chlorine amount to non-toxic lithium chloride. The thermochemical calculation indicated that no formation of magnesium chloride was recorded at nozzle exit section for the second metal hydride. Although, magnesium tends to form oxides and not chlorides at high temperature, its presence in Li-CMH compositions has enhanced the ability to eliminate HCl exhaust products. The scavenging effect reflected by the HPHS values followed the ascending trend: [LiH]<[$LiAlH_4$]<[$LiMgAlH_6$]. The incorporation of Li_4FeH_6 ternary metal hydride in composite propellant formulation showed that both lithium ad iron metals affected the HCl removal, where iron and lithium chlorides are formed during combustion.

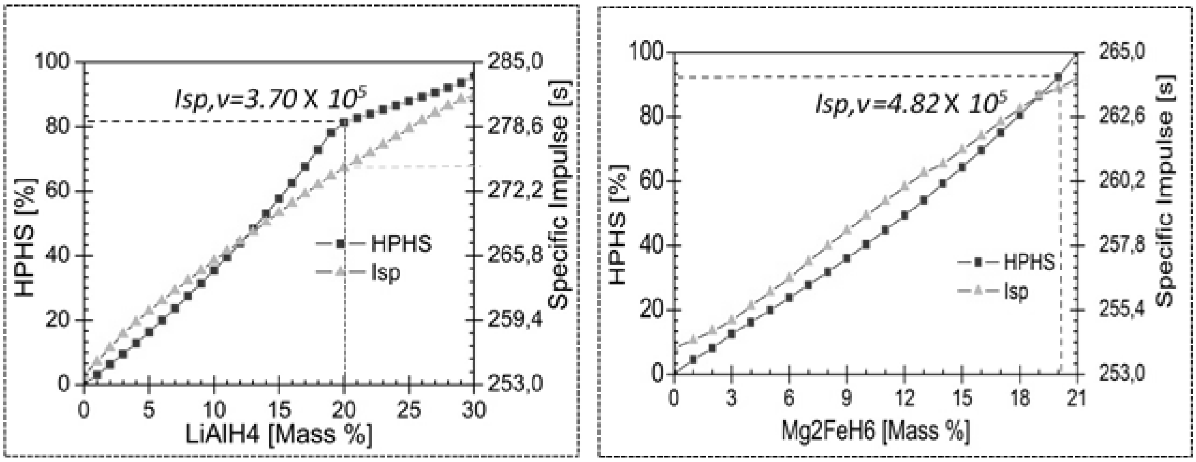


Fig. 9. Evaluation of specific impulse and its corresponding HPHS parameter value according to the additive mass fraction for the two CSPs (AP/HTPB/$LiAlH_4$ and AP/HTPB/Mg_2FeH_6).

For a deep and comprehensive understanding of the effect of two potential and promising complex metal hydrides ($LiAlH_4$ and Mg_2FeH_6) on the scavenging of HCl and performance of AP/HTPB-based propellants, several formulations have been tested to evaluate the delivered theoretical specific impulse and the calculated HPHS parameter, as shown in Fig. 9. Compared to the highest theoretical specific impulse reached by the aluminized AP/HTPB propellant containing 20 % of aluminum, which is about 263.4 s with a low HPHS value (1.5 %), propellants containing similar amount (20 %) of $LiAlH_4$ and Mg_2FeH_6 present higher HPHS values and theoretical specific impulses as shown in Fig. 9 and displayed in Table 5. The utilization of Mg_2FeH_6 as fuel allowed the improvement of the energetic performances (I_{sp}, $I_{sp,v}$) with highest removal of hydrochloric acid exhaust products (HPHS > 92 %) compared to AP/HTPB/Al propellant. The use of $LiAlH_4$, however, allowed the efficient removal of HCl products, but provided a low value of volumetric specific impulse. Consequently, these two complex metal hydrides that exhibit interesting performance with low environmental impact can be successfully incorporated to composite propellant formulations. Moreover, as shown in Fig. 7, other complex metal hydrides seem to be interesting candidate as fuel for composite propellants such as Li_3AlH_6, $LiBH_4$, $LiMgAlH_6$ and Li_3BH_6. However, the synthesis processes of such metal hydrides should be improved to decrease their excessive prices and full assessment of other properties such as compatibility, sensitivity and stability have to be undertaken in the future to fully evaluate their efficiency.

Table 5. Performances comparison of two potential halide scavenger propellants (low and high density) at 20 % of CMH fuel addition.

Propellant	HPHS [%]	I_{sp} [s]	$I_{sp,v}$ [s.kg.m^{-3}]
AP/HTPB/Al	1.5	263.4	$4.81 \cdot 10^5$
AP/ HTPB/Mg_2FeH_6	92.4	263.6	$4.82 \cdot 10^5$
AP/HTPB/ $LiAlH_4$	81.3	274.7	$3.70 \cdot 10^5$

4. Conclusions

Some promising complex metal hydrides were theoretically evaluated as high performance halide scavenger in AP-based solid propellants, meaning that they can significantly improve the ideal specific impulse and the decrease of HCl formation. This study revealed that some complex metal hydrides such as Li_4FeH_6 eliminated HCl efficiently but at the expense of the specific impulse, whereas other candidates such as $Mg(AlH_4)_2$ provided an inverse trend. Only some complex metal hydride such as Mg_2FeH_6, $LiMgAlH_6$ and $LiAlH_4$ presented a synergetic effect of high performance and high HCl scavenging effect. These latter complex metal hydrides are attractive alternatives to aluminum, resulting in a higher specific impulse and improvement to HCl emission, which can contribute to low environmental impact and exhaust plume observability. Finally, it is worthy to note that the theoretical predictions shown in the present investigation did not consider the actual feasibility of complex metal hydrides-based propellant formulations that may encounter manufacturing problems with current compounding procedures and ingredients. Furthermore, other important parameters such as compatibility, stability, sensitivity, among others have to be taken into account. The assessments require a detailed case by case study. Such kind of experimental activities is currently underway.

References

[1] A. Mezroua, K. Khimeche, M. H. Lefebvre, M. Benziane, D. Trache, The influence of porosity of ammonium perchlorate (AP) on the thermomechanical and thermal properties of the AP/polyvinylchloride (PVC) composite propellants, *J. Therm. Anal. Calorim.* **2014**, *116*, 279-286.

[2] D. Trache, T. M. Klapötke, L. Maiz, M. Abd-Elghany, L. T. DeLuca, Recent advances in new oxidizers for solid rocket propulsion, *Green Chem.* **2017**, *19*, 4711-4736.

[3] L. T. De Luca, T. Shimada, V. P. Sinditskii, M. Calabro, *Chemical rocket propulsion: A comprehensive survey of energetic materials*, Springer, **2017**.

[4] D. Trache, F. Maggi, I. Palmucci, L. T. DeLuca, K. Khimeche, M. Fassina, S. Dossi, G. Colombo, Effect of amide-based compounds on the combustion characteristics of composite solid rocket propellants, *Arab. J. Chem.* **2019**, *12*, 3639-3651.

[5] D. Trache, F. Maggi, I. Palmucci, L. T. DeLuca, Thermal behavior and decomposition kinetics of composite solid propellants in the presence of amide burning rate suppressants, *J. Therm. Anal. Calorim.* **2018**, *132*, 1601-1615.

[6] D. W. Doll, G. K. LUND, Magnesium-neutralized propellant, *J. Propul. Power.* **1992**, *8*, 1185-1191.

[7] H. Singh in *Survey of new energetic and eco-friendly materials for propulsion of space vehicles, Vol.*, Springer, **2017**, pp.127-138.

[8] G. d. Silva, S. C. Rufino, K. Iha, Green propellants: oxidizers, *J. Aerospace Technol. Manag.* **2013**, *5*, 139-144.

[9] B. C. Terry, T. R. Sippel, M. A. Pfeil, I. E. Gunduz, S. F. Son, Removing hydrochloric acid exhaust products from high performance solid rocket propellant using aluminum-lithium alloy, *J. Hazard. Mater.* **2016**, *317*, 259-266.

[10] T. M. Klapötke, N. K. Minar, J. Stierstorfer, Investigations of bis (methyltetrazolyl) triazenes as nitrogen-rich ingredients in solid rocket propellants–Synthesis, characterization and properties, *Polyhedron*. **2009**, *28*, 13-26.

[11] B. D'Andrea, F. Lillo, A. Faure, C. Perut, A new generation of solid propellants for space launchers, *Acta Astronautica*. **2000**, *47*, 103-112.

[12] A. Davenas, *Solid rocket propulsion technology*, Newnes, **2012**.

[13] F. Maggi, G. Gariani, L. Galfetti, L. T. DeLuca, Theoretical analysis of hydrides in solid and hybrid rocket propulsion, *Int. J. Hydrogen Energy.* **2012**, *37*, 1760-1769.

[14] S. Shark, T. Sippel, S. Son, S. Heister, T. Pourpoint in Theoretical performance analysis of metal hydride fuel additives for rocket propellant applications, Vol. (Ed.^Eds.: Editor), City, **2011**, pp.5556.

[15] A. R. Lawrence, J. M. Laktas, G. J. Place, P. A. Jelliss, S. W. Buckner, T. R. Sippel, Organically-Capped, Nanoscale Alkali Metal Hydride and Aluminum Particles as Solid Propellant Additives, *J. Propul. Power.* **2019**, 1-11.

[16] S. Chen, Y. Tang, H. Yu, L. Bao, W. Zhang, L. T. DeLuca, R. Shen, Y. Ye, The rapid H2 release from AlH3 dehydrogenation forming porous layer in AlH3/hydroxyl-terminated polybutadiene (HTPB) fuels during combustion, *J. Hazard. Mater.* **2019**, *371*, 53-61.

[17] L. Liu, J. Xin, F. Ma, C. Zhi, F. Li, Preparation of Magnesium-based Hydrogen Storage Materials and Their Effect on the Thermal Decomposition of Ammonium Perchlorate, *Propell. Explos. Pyrotech.* **2013**, *38*, 629-633.

[18] L. Liu, J. Li, L. Zhang, S. Tian, Effects of magnesium-based hydrogen storage materials on the thermal decomposition, burning rate, and explosive heat of ammonium perchlorate-based composite solid propellant, *J. Hazard. Mater.* **2018**, *342*, 477-481.

[19] Y.-m. Dou, Y.-j. Luo, G.-p. Li, M. Xia, Z. Ge, Thermal Decomposition Properties of Hydrogen Storage Alloy/AP/HTPB Propellants [J], *Chinese J. Explos. Propell.* **2012**, *3*.

[20] Y. Yang, F.-Q. Zhao, J. H. Yi, Y. Luo, Applications of hydrogen-storage materials in high-energy solid rocket propellants, *Chinese J. Explos. Propell.* **2015**, *38*, 8-14.

[21] L. DeLuca, L. Galfetti, F. Severini, L. Rossettini, L. Meda, G. Marra, B. D'Andrea, V. Weiser, M. Calabro, A. Vorozhtsov, Physical and ballistic characterization of AlH3-based space propellants, *Aerospace Sci.Technol.* **2007**, *11*, 18-25.

[22] W. Pang, X. Fan, F. Zhao, H. Xu, W. Zhang, H. Yu, Y. Li, F. Liu, W. Xie, N. Yan, Effects of Different Metal Fuels on the Characteristics for HTPB-based Fuel Rich Solid Propellants, *Propell. Explos. Pyrotech.* **2013**, *38*, 852-859.

[23] B. C. Terry, S. F. Son, I. E. Gunduz in Solid-rocket Propellants, Vol. US20180079697A1 (Ed.^Eds.: Editor), Purdue Research Foundation, City, **2018**.

[24] G. Nechiporenko, D. Lempert, An analysis of energy potentialities of composite solid propellants containing beryllium or beryllium hydride as an energetic component, *Chem. Phys. Reports*. **1998**, *17*, 1927-1947.

[25] N. Rusman, M. Dahari, A review on the current progress of metal hydrides material for solid-state hydrogen storage applications, *Int. J. Hydrogen Energy*. **2016**, *41*, 12108-12126.

[26] X. Huang, S. Li, X. Zheng, S. Yang, Y. Guo, Combustion mechanism of a novel energetic fuel candidate based on amine metal borohydrides, *Energy & Fuels*. **2016**, *30*, 1383-1389.

[27] L. Jin, P. Du, M. Yao, The influence of magnesium hydride on the thermal decomposition properties of nitrocellulose, *J. Energ. Mater.* **2014**, *32*, S13-S21.

[28] D. Lempert, G. Nechiporenko, G. Manelis, Energetic capabilities of high-density composite solid propellants containing zirconium or its hydride, *Combust, Explos. Shock Waves*. **2011**, *47*, 45-54.

[29] Y. Yang, F. Zhao, H. Xu, Q. Pei, H. Jiang, J. Yi, C. Xuan, S. Chen, Hydrogen-enhanced combustion of a composite propellant with ZrH2 as the fuel, *Combust. Flame*. **2018**, *187*, 67-76.

[30] M. B. Ley, L. H. Jepsen, Y.-S. Lee, Y. W. Cho, J. M. B. Von Colbe, M. Dornheim, M. Rokni, J. O. Jensen, M. Sloth, Y. Filinchuk, Complex hydrides for hydrogen storage–new perspectives, *Mater. Today*. **2014**, *17*, 122-128.

[31] K. Møller, D. Sheppard, D. Ravnsbæk, C. Buckley, E. Akiba, H.-W. Li, T. Jensen, Complex metal hydrides for hydrogen, thermal and electrochemical energy storage, *Energies*. **2017**, *10*, 1645.

[32] W. Zhang, Z. Zhang, X. Jia, J. Guo, J. Wang, P. Chen, Metathesis of Mg 2 FeH 6 and LiNH 2 leading to hydrogen production at low temperatures, *Phys. Chem. Chem. Phys.* **2018**, *20*, 9833-9837.

[33] L. Fohlmeister, A. Stasch, Alkali metal hydride complexes: well-defined molecular species of saline hydrides, *Aust. J. Chem.* **2015**, *68*, 1190-1201.

[34] C. M. Beighley, W. R. Fish, R. E. Anderson in *Advanced Fuels and Oxidizers, Vol.*, Springer, **1970**, pp.163-189.

[35] G. Singh, *Recent advances on energetic materials*, Nova Science Publishers, Incorporated, **2015**.

[36] D. Frem, A Reliable Method for Predicting the Specific Impulse of Chemical Propellants, *J. Aerospace Technol. Manag.* **2018**, *10*.

[37] M. H. Keshavarz, Prediction method for specific impulse used as performance quantity for explosives, *Propell. Explos. Pyrotech.* **2008**, *33*, 360-364.

[38] L. DeLuca, L. Galfetti, G. Colombo, F. Maggi, A. Bandera, V. Babuk, V. Sinditskii, Microstructure effects in aluminized solid rocket propellants, *J. Propul. Power.* **2010**, *26*, 724-732.

[39] B. J. McBride, *Computer program for calculation of complex chemical equilibrium compositions and applications*, NASA Lewis Research Center, **1996**.

[40] S. Gordon, B. J. McBride, Computer program for calculation of complex chemical equilibrium compositions and applications. Part 1: Analysis. **1994**.

[41] N. Kubota, *Propellants and explosives: thermochemical aspects of combustion*, John Wiley & Sons, **2015**.

[42] H. Saitoh, S. Takagi, M. Matsuo, Y. Iijima, N. Endo, K. Aoki, S.-i. Orimo, Li4FeH6: Iron-containing complex hydride with high gravimetric hydrogen density, *APL Mater.* **2014**, *2*, 076103.

[43] Y. X. Qiu, L. De-Li, S. Ge, A. Bing-Yun, Electronic structures and thermodynamic stabilities of aluminum-based deuterides from first principles calculations, *Chinese Phys. B.* **2011**, *20*, 017102.

[44] L. George, V. Drozd, A. Durygin, J. Chen, S. K. Saxena, Bulk modulus and thermal expansion coefficient of mechano-chemically synthesized Mg2FeH6 from high temperature and high pressure studies, *Int. J. Hydrogen Energy*. **2009**, *34*, 3410-3416.

[45] H. Grove, O. M. Løvvik, W. Huang, S. M. Opalka, R. H. Heyn, B. C. Hauback, Decomposition of lithium magnesium aluminum hydride, *Int. J. Hydrogen Energy*. **2011**, *36*, 7602-7611.

[46] M. Van Setten, G. De Wijs, V. Popa, G. Brocks, Ab initio study of Mg (Al H 4) 2, *Phys. Review B*. **2005**, *72*, 073107.

[47] W. Atwell, K. Rojdev, D. Liang, M. Hill, Metal Hydrides, MOFs, and Carbon Composites as Space Radiation Shielding Mitigators. **2014**.

[48] P. Fornasiero, M. Graziani, *Renewable resources and renewable energy: a global challenge*, CRC press, **2011**.

[49] K. T. Møller, D. Sheppard, D. B. Ravnsbæk, C. E. Buckley, E. Akiba, H.-W. Li, T. R. Jensen, Complex metal hydrides for hydrogen, thermal and electrochemical energy storage, *Energies*. **2017**, *10*, 1645.

[50] A. Andreasen, Predicting formation enthalpies of metal hydrides, *Ris National Laboratory Report*. **2004**.

[51] G. Walker, *Solid-state hydrogen storage: materials and chemistry*, Elsevier, **2008**.

[52] H. Grove, H. W. Brinks, O. M. Løvvik, R. H. Heyn, B. C. Hauback, The crystal structure of LiMgAlD6 from combined neutron and synchrotron X-ray powder diffraction, *J. Alloys Compd.* **2008**, *460*, 64-68.

[53] F. J. Hendel, Review of solid propellants for space exploration. **1965**.

[54] A. Gany, D. W. Netzer, Fuel performance evaluation for the solid-fueled ramjet, *Int. J. Turbo Jet Engines*. **1985**, *2*, 157-168.

[55] M. Polanski, T. K. Nielsen, Y. Cerenius, J. Bystrzycki, T. R. Jensen, Synthesis and decomposition mechanisms of Mg2FeH6 studied by in-situ synchrotron X-ray diffraction and high-pressure DSC, *Int. J. Hydrogen Energy.* **2010**, *35*, 3578-3582.

[56] S. L. Suib, *New and future developments in catalysis: batteries, hydrogen storage and fuel cells*, Newnes, **2013**.

[57] B. Li, J. Li, H. Shao, L. He, Mg-Based Hydrogen Absorbing Materials for Thermal Energy Storage—A Review, *App. Sci.* **2018**, *8*, 1375.

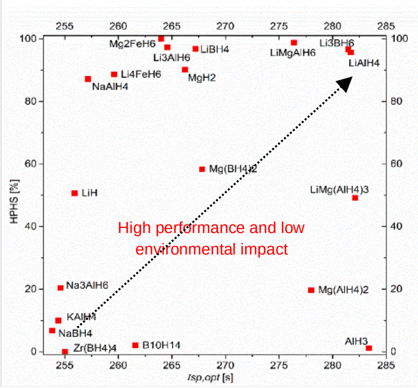
[58] X. Zhang, W. Tian, J. Yang, R. Yang, J. Zheng, X. Li, Synthesis and hydrogen storage behaviour of pure Mg2FeH6 at nanoscale, *Materials transactions*. **2011**, *52*, 618-622.

[59] S. Brutti, L. Farina, F. Trequattrini, O. Palumbo, P. Reale, L. Silvestri, S. Panero, A. Paolone, Extremely pure Mg2FeH6 as a negative electrode for lithium batteries, *Energies*. **2018**, *11*, 1952.

Entry for the Table of Contents

FULL PAPER

This paper offers a theoretical analysis concerning the employment of metal hydrides as efficient additives to mitigate some of the negative effects of HCl on the environment during the combustion of AP-based composite propellants. It is reveals that complex metal hydrides-based propellants exhibited a synergetic effect of high specific impulse and low environmental impact. Thus, a good choice of metal hydride can provide clean/green propellant formulations that can satisfy the current environmental requirements with better performance than current aluminium propellants.



*Author(s), Corresponding Author(s)**

Page No.1 – Page No.24

Effect of complex metal hydrides on the elimination of hydrochloric acid exhaust products from high-performance composite solid propellants: A theoretical analysis