

FFI RAPPORT

COMBUSTION OF RS-41

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FFI/RAPPORT-2000/02758

FFIBM/778/130

Approved
Kjeller 25 May 2000

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Director of Research

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FORSVARETS FORSKNING SINSTITUTT (FFI)
Norwegian Defence Research Establishment

UNCLASSIFIED

P O BOX 25
NO-2027 KJELLER, NORWAY
REPORT DOCUMENTATION PAGE

SECURITY CLASSIFICATION OF THIS PAGE
(when data entered)

1) PUBL/REPORT NUMBER FFI/RAPPORT-2000/02758	2) SECURITY CLASSIFICATION UNCLASSIFIED	3) NUMBER OF PAGES 23
1a) PROJECT REFERENCE FFIBM/778/130	2a) DECLASSIFICATION/DOWNGRADING SCHEDULE -	
4) TITLE COMBUSTION OF RS-41		
5) NAMES OF AUTHOR(S) IN FULL (surname first) MOXNES John F, NEVSTAD Gunnar Ove, ERIKSEN Svein W		
6) DISTRIBUTION STATEMENT Approved for public release. Distribution unlimited. (Offentlig tilgjengelig)		
7) INDEXING TERMS IN ENGLISH:		
a) <u>Pyrotechnic</u>	IN NORWEGIAN:	
b) <u>Combustion</u>	a) <u>Pyroteknik</u>	
c) <u>Closed Vessel</u>	b) <u>Forbrenning</u>	
d) <u>Multipurpose</u>	c) <u>Lukket bombe</u>	
e) <u>Oxidation</u>	d) <u>Multipurpose</u>	
	e) <u>Oksidasjon</u>	
THESAURUS REFERENCE:		
8) ABSTRACT <p>The pyrotechnic composition RS-41, a mixture of 49 wt.% KClO₄, 49 wt.% Al/Mg and 2 wt.% Calcium Resinate, is an important ingredient in the MP (Multipurpose) ammunition. RS-41 placed in the front of the projectile ignites due to impulse transfer by impact. A pyrotechnically combustion starts and spreads backward in the projectile and towards the explosive. This gives a delay that is important for the fragmentation effect of the warhead.</p> <p>This report do analyses Closed Vessel experiments performed on RS-41. In addition we try to give a consistent description of the chemical conditions in the Closed Vessel.</p>		
9) DATE 25 May 2000	AUTHORIZED BY This page only Bjarne Haugstad	POSITION Director of Research

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SECURITY CLASSIFICATION OF THIS PAGE
(when data entered)

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COMBUSTION OF RS-41

1 INTRODUCTION

The pyrotechnic composition RS-41, a mixture of 49 wt.% KClO_4 , 49 wt.% Al/Mg and 2 wt.% Calcium Resinate, is an important ingredient in the MP (Multipurpose) ammunition. RS-41 placed in the front of the projectile ignites due to impulse transfer by impact. A pyrotechnical combustion starts and spreads backward in the projectile and towards the explosive. This gives a delay that is important for the fragmentation effect of the warhead.

This report investigates Closed Vessel experiments performed on RS-41, and in addition we try to give a consistent description of the chemical conditions in the Closed Vessel.

2 EXPERIMENTALLY

The compositions have been tested in a 150 cm^3 Closed Vessel. Ignition has been performed with a brown/blue squib and 2 gram of Black powder. The pressure has been measured with a Kistler 6211 high-pressure Quartz Sensor. Sampling rate of the pressure points has been from $1 \mu\text{s}$ and longer. Maximum number of pressure points has been 66000.

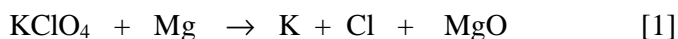
3 DISSCUSION

3.1 50 % Mg, 50 % KClO_4

3.1.1 Approximate analyse

An understanding of what is happening in the combustion of RS-41 is established by studying different simpler combinations of the ingredients. Our first situation is a composition containing equal weight fractions of magnesium powder and potassium perchlorate crystals.

A simple decomposition can be written by [1]



Let M_{TOT} be the total mass of the combination. We then have:

$$N_{\text{Cl}}^0 \cdot m_{\text{Cl}} + N_{\text{K}}^0 \cdot m_{\text{K}} + N_{\text{O}}^0 \cdot m_{\text{O}} = 0.5 \cdot M_{\text{TOT}}$$

Where;

N_{Cl}^0 = number of Cl atoms, m_{Cl} = mass of Cl atoms.

N_{K}^0 = number of K atoms, m_{K} = mass of K atoms.

N_O^0 = number of O atoms, m_O = mass of O atoms.

N_{Mg}^0 = number of Mg atoms, m_{Mg} = mass of Mg atoms.

N_{Al}^0 = number of Al atoms, m_{Al} = mass of Al atoms

Now we have:

$$N_{Cl}^0 = N_K^0 = \frac{1}{4} N_O^0 \quad \text{and} \quad N_{Cl}^0 = N_K^0 = \frac{0.5 \cdot M_{TOT}}{m_{Cl} + m_K + 4 \cdot m_O}$$

The number of Mg particles is given by (initially)

$$N_{Mg}^0 = 0.5 \cdot M_{TOT} / m_{Mg} = 20.572 \text{ mol/kg} \cdot M_{TOT} N_A, \text{ where } N_A \text{ is Avogadro's number}$$

The number of particles is given by (initially)

$$N_{Mg}^0 = 4N_{Cl}^0 = \frac{2 \cdot M_{TOT}}{m_{Cl} + m_K + 4 \cdot m_O}$$

Then the ratio between Mg and O will be:

$$N_{Mg}^0 / N_O^0 = \frac{m_{Cl} + m_K + 4 \cdot m_O}{4 \cdot m_{Mg}} = 1.425$$

All oxygen can then react with Mg. Some Mg will not have reacted.

We then have that:

$$N_{MgO} = N_O^0 = \frac{2 \cdot M_{TOT}}{m_{Cl} + m_K + 4m_O}$$

The number of moles MgO is then given by:

$$n_{MgO} = \left[\frac{2 \cdot M_{TOT}}{m_{Cl} + m_K + 4m_O} \right] / N_A,$$

$$n_{MgO} = \frac{2 \cdot M_{TOT}}{138.55 \cdot 10^{-3} \text{ kg/mol}} = 14.435 \text{ mol/kg} \cdot M_{TOT}$$

$$n_{Cl} = \frac{0.5 \cdot M_{TOT}}{[m_{Cl} + m_K + 4 \cdot m_O] \cdot N_A} = 3.609 \text{ mol/kg} \cdot M_{TOT}$$

$$n_K = n_{Cl}$$

We have some rests of Mg:

$$n_{Mg} = \frac{N_{Mg}}{N_A} = \frac{N_{Mg}^0 - N_O^0}{N_A} = \left[\frac{0.5 \cdot M_{TOT}}{m_{Mg}} - \frac{2 \cdot M_{TOT}}{m_{Cl} + m_K + 8m_O} \right] / N_A = 6.137 \text{ mol/kg} \cdot M_{TOT}$$

This gives:

$$n_{Mg} = 6.137 \text{ mol/kg} \cdot M_{TOT}$$

The pressure of the reaction products in [1], if we do not include the covolume, will then be:

$$P = (n_{Cl} + n_K + n_{Mg}) \cdot RT / V$$

where

$$V = 15 \cdot 10^{-4} m^3 \text{ for the Closed Vessel.}$$

By selecting a temperature (T=3600 K) close to the boiling point for MgO we then have when $M_{TOT} = 1.8 \cdot 10^{-2} \text{ kg}$:

$$P = 48 \text{ MPa}$$

Experimentally measured pressures is 48 MPa.

3.1.2 Cheetah calculations

Calculations by use of the CHEETAH code (1) gives also another solution where Mg exists as solid or liquid inside the oxidised particles.

Let x be the Mg part of the total mass that participate in the reaction. We then have:

$$M_{TOT} = 0.5 \cdot M_{TOT} + (0.5 - x) \cdot M_{TOT} + x \cdot M_{TOT}$$

$KClO_4$
inactive
active

The ratio between active Mg and $KClO_4$ is then:

$$F = x/0.5$$

The total density is given by $\rho = M_{TOT}/V$.

Density of active material is given by:

$$\rho_A = [0.5 \cdot M_{TOT} + F \cdot 0.5 \cdot M_{TOT}] / V = 0.5 \cdot [1 + F] \cdot \rho$$

We have also to take into consideration that the gas particles cannot occupy the volume of the solid (liquid) Mg. We therefor correct the pressure given by the Cheetah programme by the following factor:

$$1 / \left(1 - \frac{\rho}{\rho_{Mg}} \cdot 0.5(1 - F) \right)$$

Figure 3.1 and 3.2 show the Cheetah pressure and the pressure when corrected for the volume of the inactive Mg given as function of load density. In addition, the figure containing the experimentally

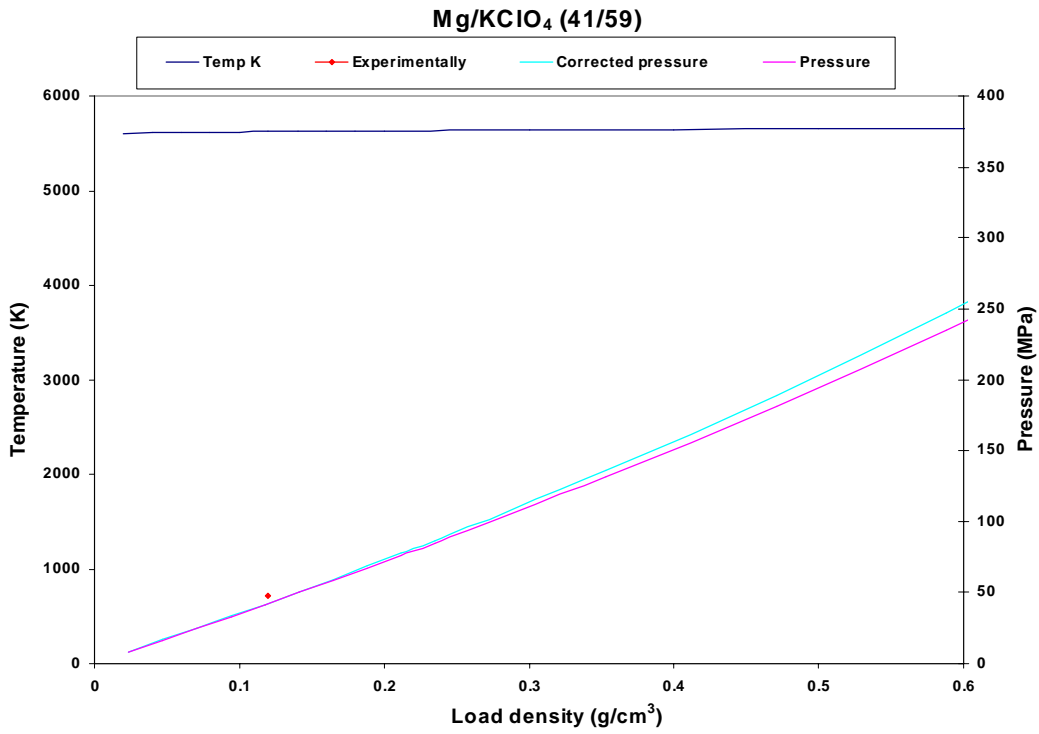


Figure 3.1 Temperature and pressure as function of load density for Mg/KClO₄.

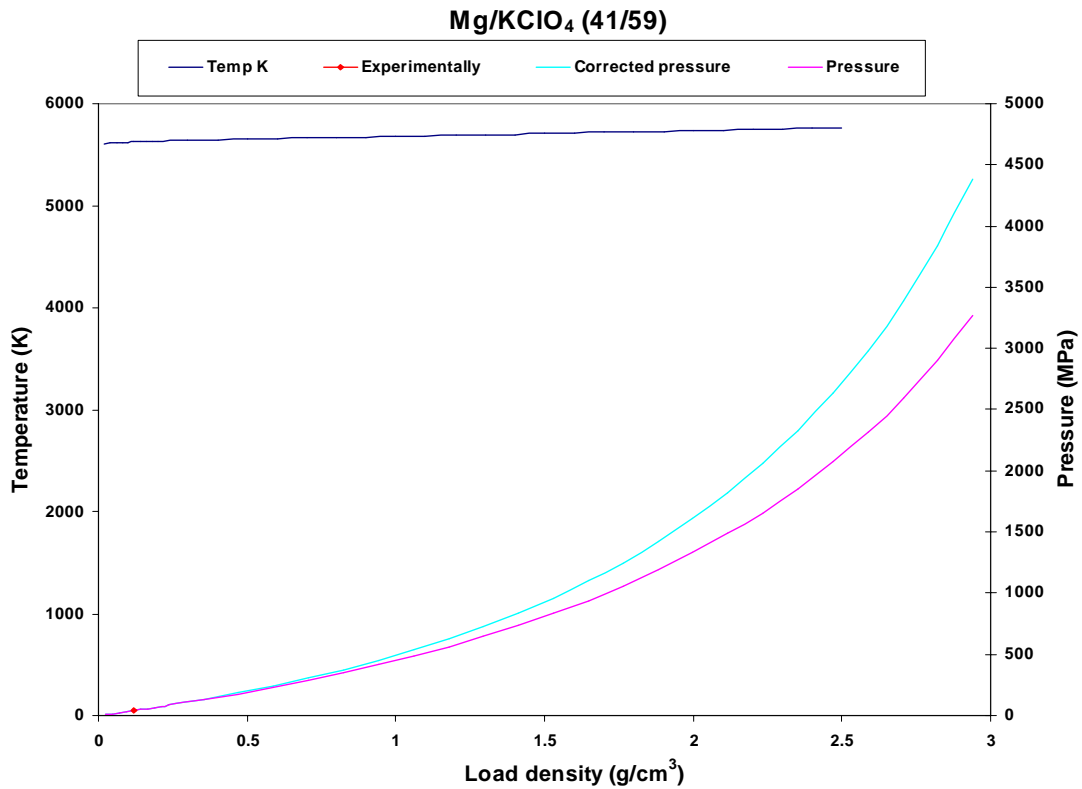


Figure 3.2 Temperature and pressures as function of load density for Mg/KClO₄.

Mg/KClO₄ (41/59)

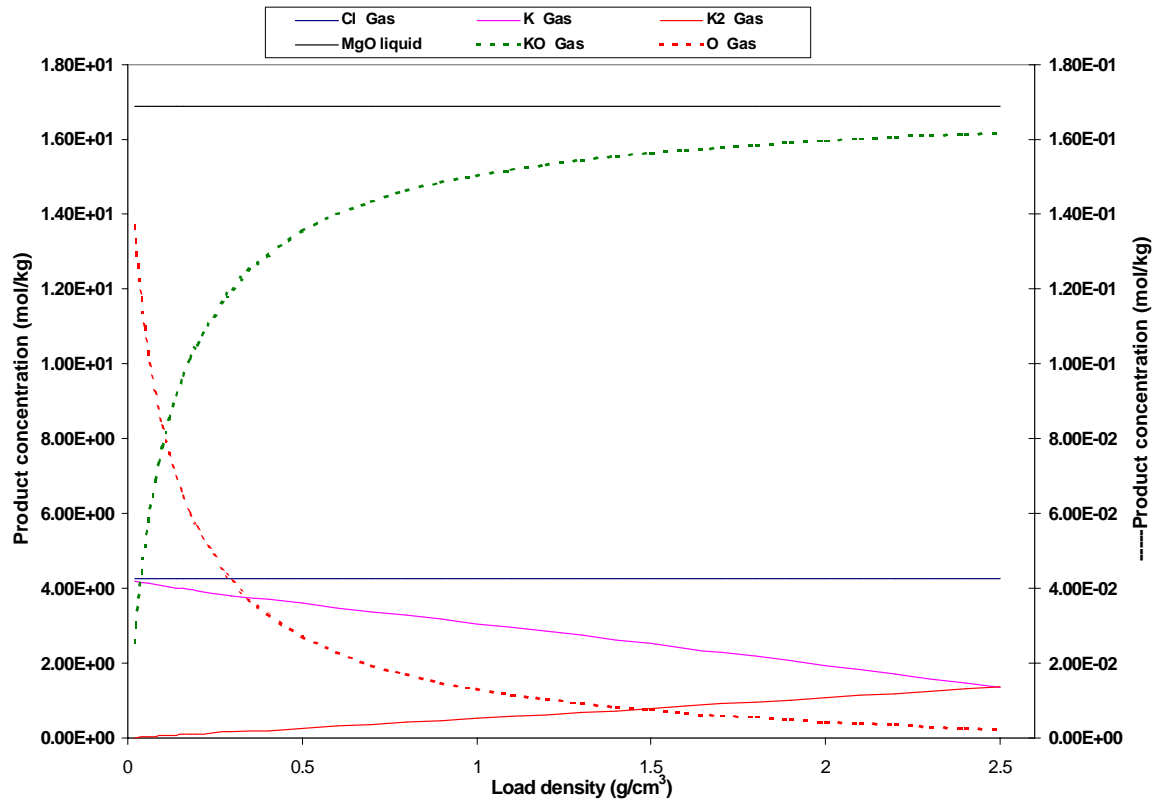


Figure 3.3 Product composition and concentrations as function of load density for Mg/KClO₄ calculated by use of Cheetah.

measured pressure. We can observe in Figure 3.1 that agreement with the experimental results is achieved.

An approximation for the co-volume is obtained by setting :

$$V_C \approx M_{TOT}/\rho_{TMD}$$

where ρ_{TMD} is the maximum density.

With ρ_{TMD} is $\sim 2 \cdot 10^3$ kg/m³ we then get

$$V_C/V \sim 0.06$$

For our load density the co-volume does has an effect of 6%.

We terminate this section with the following conclusions:

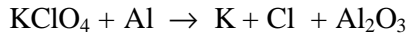
- I. All the oxygen did react with the magnesium.
- II. The K and Cl products are in the gas phase.
- III. Rest Mg is either in the gas phase or lays as liquid or solid in the core of the oxidised particles.

3.2 50% KClO_4 + 50% Al

3.2.1 Approximate analyse

We will now look at the situation where we have equal amounts of aluminium powder and potassium perchlorate (KClO_4). It will soon be clear that this case will require a more complicated analysis.

A simple decomposition is shown below:



We have the same situation as in 3.1.1 that:

$$N_{\text{Cl}}^0 = N_{\text{K}}^0 = \frac{0.5 \cdot M_{\text{TOT}}}{m_{\text{Cl}} + m_{\text{K}} + 4m_{\text{O}}} = \frac{1}{4} N_{\text{O}}^0$$

The number of aluminium particles are given by;

$$N_{\text{Al}}^0 = \frac{0.5 \cdot M_{\text{TOT}}}{m_{\text{Al}}} = 18.53 \text{ mol/kg} \cdot M_{\text{TOT}} \cdot N_{\text{A}}$$

The ratio between aluminium and oxygen atoms is:

$$N_{\text{Al}}^0 / N_{\text{O}}^0 = \frac{m_{\text{Cl}} + m_{\text{K}} + 4 \cdot m_{\text{O}}}{4 \cdot m_{\text{Al}}} = 1.284$$

Since the ratio is higher than 2/3, it is clear that all oxygen can react with aluminium, and in addition there will still be some aluminium left over.

We therefor have:

$$N_{\text{Al}_2\text{O}_3} = \frac{1}{3} N_{\text{O}}^0 = \frac{2 \cdot M_{\text{TOT}}}{3(m_{\text{Cl}} + m_{\text{K}} + 4m_{\text{O}})}$$

The number of moles aluminium consumed by the oxygen to produce Al_2O_3 is given by:

$$n_{\text{Al}_2\text{O}_3} = \frac{2}{3} \cdot \frac{M_{\text{TOT}}}{138.55 \cdot 10^{-3} \text{ kg/mol}} = 4.81 \text{ mol/kg} \cdot M_{\text{TOT}}$$

$$n_{\text{Cl}} = n_{\text{K}} = 3.61 \text{ mol/kg}$$

This gives us a rest of aluminium of:

$$n_{Al} = \frac{N_{Al}}{N_A} = \frac{N_{Al}^0 - 2N_{Al_2O_3}}{N_A} = \frac{0.5 \cdot M_{TOT} - \frac{4M_{TOT}}{3 \cdot (m_{Cl} + m_K + 4 \cdot m_O)}}{N_{Al}} = 8.91 \text{ mol/kg} \cdot M_{TOT}$$

The pressure is now, if we set the temperature close to the boiling point of Al_2O_3 (3250 K) and $M_{TOT} = 1.8 \cdot 10^{-2} \text{ kg}$:

$$P = (n_{Cl} + n_K + n_{Al}) \cdot R \cdot T / V = 52 \text{ MPa}$$

while experimentally measured pressure was 35 MPa.

The difference between experimentally measured and above calculated pressure is significant. However, observe that K and Cl together gives a pressure of;

$$P = (n_{Cl} + n_K) \cdot R \cdot T / V = 23 \text{ MPa}$$

As a solution we will now recommend that part of the Al lays in the core of the particles, and is not in the gas phase. As a result the temperature in the Closed Vessel will not be homogeneous. This gives us the following equation for aluminium in the gas phase:

$$(n_{Cl} + n_K + n'_{Al}) \cdot R \cdot T / V = 35 \text{ MPa}$$

$$n'_{Al} = 35 \times 10^6 \times 1.5 \times 10^{-4} / 8.319 / 3250 - n_{Cl} - n_K = 0.0658 \text{ mol}$$

and

$$n'_{Al} = 0.0658 \text{ mol} / 1.8 \times 10^{-3} \text{ kg} = 3.66 \text{ mol/kg} \times M_{TOT}$$

By comparing n'_{Al} with n_{Al} gives that 59% of n_{Al} does not form gas. Of the total aluminium mass we then get the following ratio as inactive:

$$0.59 \cdot 8.91 / 18.53 = 0.28$$

28% of the total aluminium mass does neither give pressure or react (is inactive).

Based on the above approximate analysis, we have concluded that 28% of the total Al mass does not give any support to the reaction.

3.2.2 Cheetah calculations

Let x be the aluminium part of the total mass that participate in the reaction. We have then

$$M_{TOT} = 0.5 \cdot M_{TOT} + (0.5 - x) \cdot M_{TOT} + x \cdot M_{TOT}$$

$KClO_4$ inactive active

The ratio between active Al and $KClO_4$ is then:

$$F = x/0.5$$

Total density is given by: $\rho = M_{TOT} / V$

Density of active material is given by:

$$\rho_A = [0.5 \cdot M_{TOT} + F \cdot 0.5 \cdot M_{TOT}] / V = 0.5 \cdot \rho \cdot [1 + F]$$

Figure 3.4 and 3.5 show the Cheetah calculated temperature and pressures as function of load density $\rho = \rho_A / 0.5(1 + F)$. In addition the figures show the experimentally measured pressure.

We have also to take into consideration that the gas particles cannot occupy the volume of the solid and liquid Al. We therefore correct the pressure given by the Cheetah programme by the following factor:

$$1 / \left(1 - \frac{\rho}{\rho_{Al}} \cdot 0.5(1 + F) \right)$$

We can see from Figure 3.4 that when $F=0.25$ (20/80), best agreement with the experimental result is achieved.

This gives that 75% of the aluminium neither takes part in the oxidation or give support to the gas pressure (is inactive). Figure 3.5 shows the same curves as Figure 3.4 but for higher load densities. Observe that use of all oxygen to the oxidation of the aluminium requires a ratio of 33/67 between reacted aluminium and potassium perchlorate. A 20/80 ratio indicates then that some of the aluminium does not have access to the oxygen. We anticipate that the reason is due to an oxide layer around the particles.

Temperatures and pressures for Al/KClO₄ compositions at different load densities

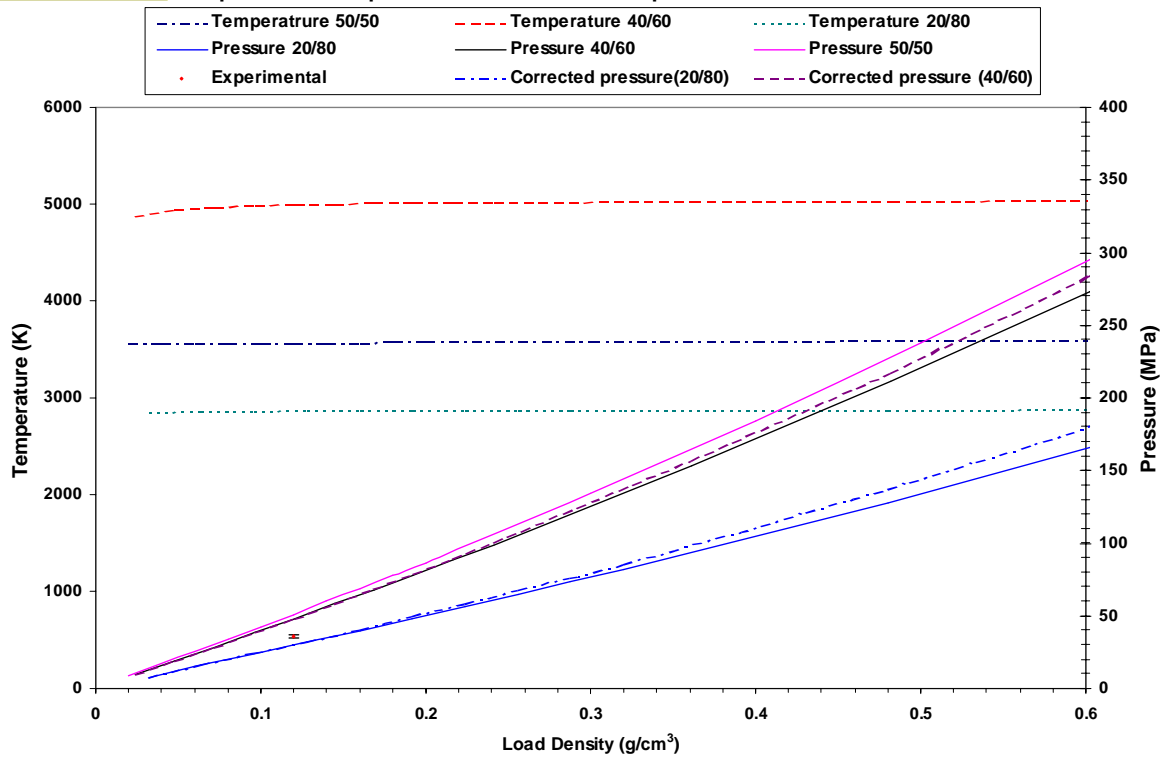


Figure 3.4 Temperature and pressure for different Al/KClO₄ compositions as function of load density ρ .

Temperatures and pressures for Al/KClO₄ compositions at different load densities

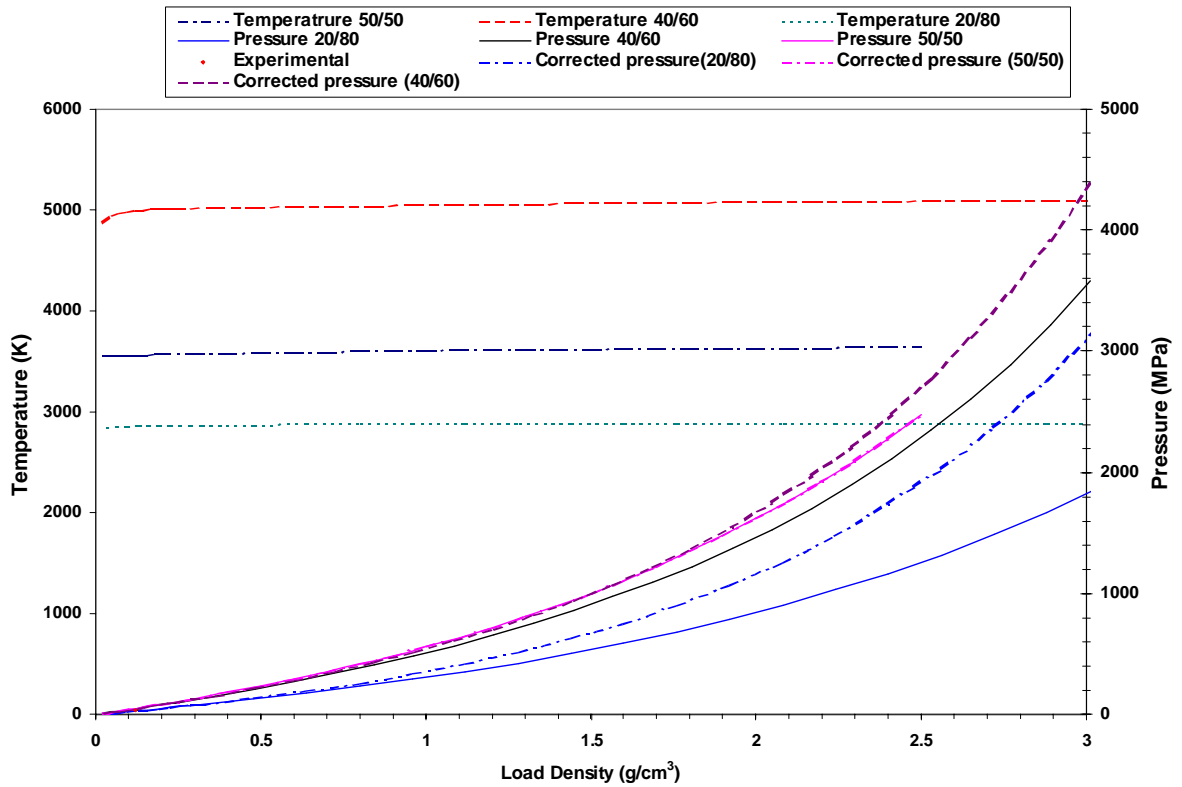


Figure 3.5 Temperature and pressure for different Al/KClO₄ compositions as function of load density ρ .

Figure 3.6 shows the product composition based on the Cheetah calculations. We observe that the situation at equilibrium is complex.

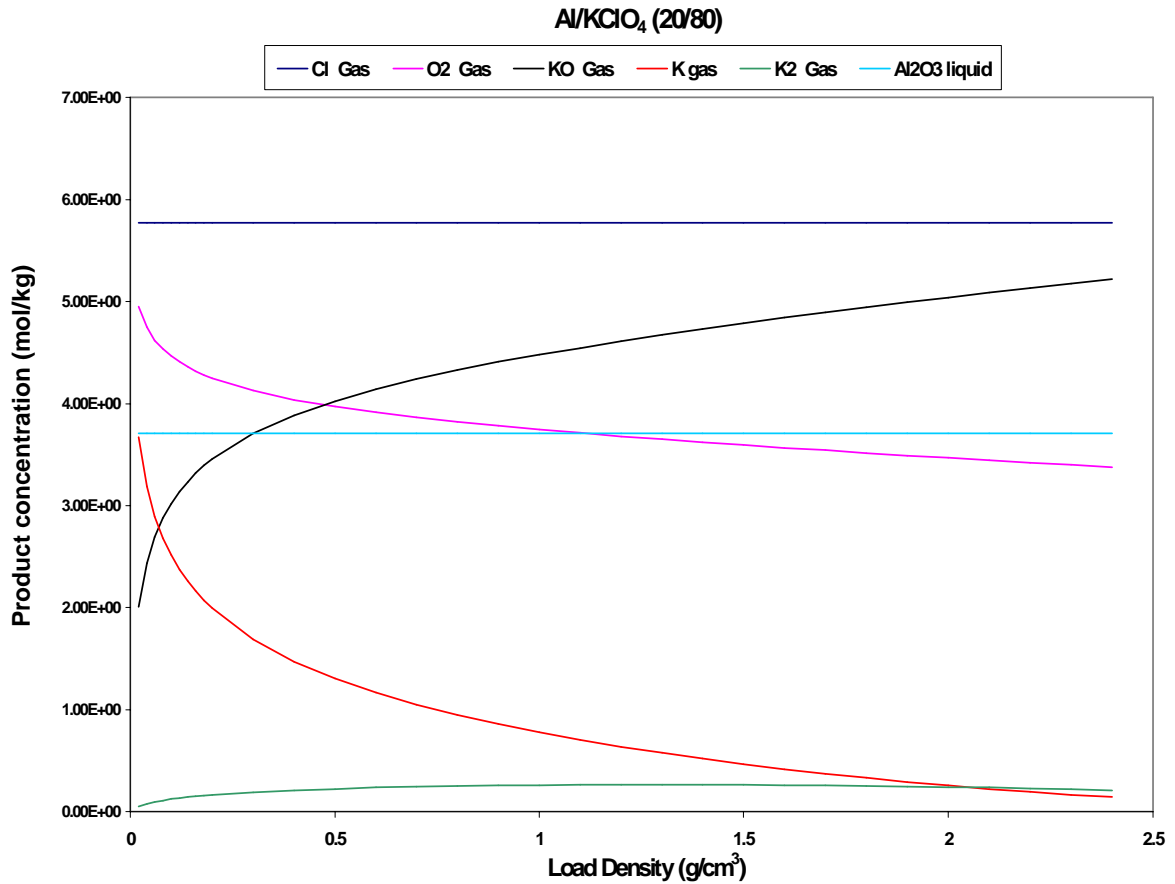


Figure 3.6 Concentrations of products of the composition Al/KClO₄ (20/80) at different load densities ρ .

We finish this section by the following conclusions:

- I. The temperature in the Closed Vessel seems not be homogeneous but contains aluminium in solid or liquid phase in the core of the oxidised particles
- II. The temperature is close to the boiling point for Al₂O₃ (3250 K).
- III. 75% of the Al is to be considered as inert.

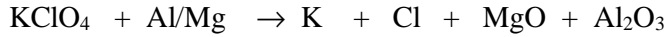
We will also add that the first conclusions above is supported by an extended analysis of the residue content in the Closed Vessel. The rests indicated that the particles consist of an internal core (Al) with an outer oxide layer.

3.3 50% KClO₄, 25% Al, 25% Mg

We consider now the two component material 50% KClO₄ and 50% Al/Mg. The Al/Mg alloy consist of 50% Al and 50% Mg.

In the analysis in chapter 3.2 our conclusion were that 75% of the Al in the core of the oxidised particles were in the liquid or solid phase. This involved a lower pressure than what a homogeneous equilibrium state should indicate.

Under low temperature oxidising of Al/Mg particles we did observe that most of the Mg was oxidised before Al. We will anticipate the following reaction route:



We have as in chapter 3.1 and 3.2 that:

$$N_{\text{Cl}}^0 = N_{\text{K}}^0 = \frac{1}{4} \cdot N_{\text{O}}^0$$

We have that the number of Mg particles is:

$$N_{\text{Mg}}^0 = 0.25 \cdot M_{\text{TOT}} / m_{\text{Mg}}$$

The number of oxygen atoms is:

$$N_{\text{Al}}^0 = \frac{0.25 \cdot M_{\text{TOT}}}{m_{\text{Al}}} = 9.266 \text{ mol/kg} \cdot M_{\text{TOT}} \cdot N_{\text{A}}$$

This gives us that:

$$N_{\text{O}}^0 = 4 \cdot N_{\text{Cl}}^0 = \frac{2 \cdot M_{\text{TOT}}}{m_{\text{Cl}} + m_{\text{K}} + 4 \cdot m_{\text{O}}}$$

$$N_{\text{Mg}}^0 / N_{\text{O}}^0 = \frac{0.25 \cdot (m_{\text{Cl}} + m_{\text{K}} + m_{\text{O}})}{2 \cdot m_{\text{Mg}}} = 0.71$$

We will then anticipate that all Mg particles will be oxidised to MgO.

$$N_{\text{MgO}} = N_{\text{Mg}}^0 = \frac{0.25 \cdot M_{\text{TOT}}}{m_{\text{Mg}}} = 10.28 \text{ mol/kg} \cdot M_{\text{TOT}} \cdot N_{\text{A}}$$

$$n_{\text{Cl}} = n_{\text{K}} = 3.61 \text{ mol/kg} \cdot M_{\text{TOT}}$$

Residual oxygen will react with aluminium. This gives us:

$$N_{\text{O}} = N_{\text{O}}^0 - N_{\text{MgO}} = \frac{2 \cdot M_{\text{TOT}}}{m_{\text{Cl}} + m_{\text{K}} + 4 \cdot m_{\text{O}}} - \frac{0.25 \cdot M_{\text{TOT}}}{m_{\text{Mg}}} = 4.151 \text{ mol/kg} \cdot M_{\text{TOT}} \cdot N_{\text{A}}$$

$$N_{\text{Al}_2\text{O}_3} = \frac{1}{3} N_{\text{O}} = 1.38 \text{ mol/kg} \cdot M_{\text{TOT}}$$

$$n_{\text{Al}_2\text{O}_3} = 1.38 \text{ mol/kg} \cdot M_{\text{TOT}}$$

The rest of the aluminium is given by:

$$N_{Al} = N_{Al}^0 - 2 \cdot N_{Al_2O_3} = \frac{0.25 \cdot M_{TOT}}{m_{Al}} - \frac{2}{3} \cdot 1.38 \text{ mol/kg} \cdot M_{TOT} \cdot N_A$$

$$n_{Al} = \frac{0.25 \cdot M_{TOT}}{m_{Al}} - 2.77 \text{ mol/kg} \cdot M_{TOT} = 6.50 \text{ mol/kg} \cdot M_{TOT}$$

By assuming that $T = 3250 \text{ K}$, we now get the following pressure:

$$P = (n_{Cl} + n_K + n_{Al}) \cdot R \cdot T / V = 44 \text{ MPa}$$

Experimentally the pressure was measured to be 35 MPa .

Without Al gas we get:

$$P = (n_{Cl} + n_K) \cdot R \cdot T / V = 23 \text{ MPa}$$

We will again assume that some of the aluminium is in solid or liquid state inside the particles. This gives us the following equation:

$$(n_{Cl} + n_K + n'_{Al}) \cdot R \cdot T \cdot V = 35 \text{ MPa}$$

This give:

$$n'_{Al} = 0.0658 \text{ mol} = 3.65 \text{ mol/kg} \cdot M_{TOT}$$

Comparing of n'_{Al} and n_{Al} gives that 44% of the n_{Al} does not contribute to the gaseous products. Of the total aluminium mass we get then an inactive part of:

$$0.45 \cdot 6.5 / 9.266 = 0.31$$

3.3.1 Cheetah calculations

We have used the Cheetah code to perform a more accurate analysis of the reaction. We let x be that part of the aluminium of the total mass content which is inactive. This gives us the following equation:

$$M_{TOT} = 0.5 \cdot \underset{\text{KClO}_4}{B} M_{TOT} + 0.25 \cdot \underset{\text{Active Mg}}{B} M_{TOT} + 0.25 \cdot x \cdot \underset{\text{Inactive Al}}{B} M_{TOT} + x \cdot \underset{\text{Active Al}}{B} M_{TOT}$$

The ratio between active aluminium and potassium perchlorate is given by:

$$F = x / 0.5$$

The density of the material that is active is now given by:

$$\rho_A = \rho \cdot (1 + 0.5 + F) \cdot 0.5$$

Figure 3.7 shows pressure and temperature as function of load density. The density is:

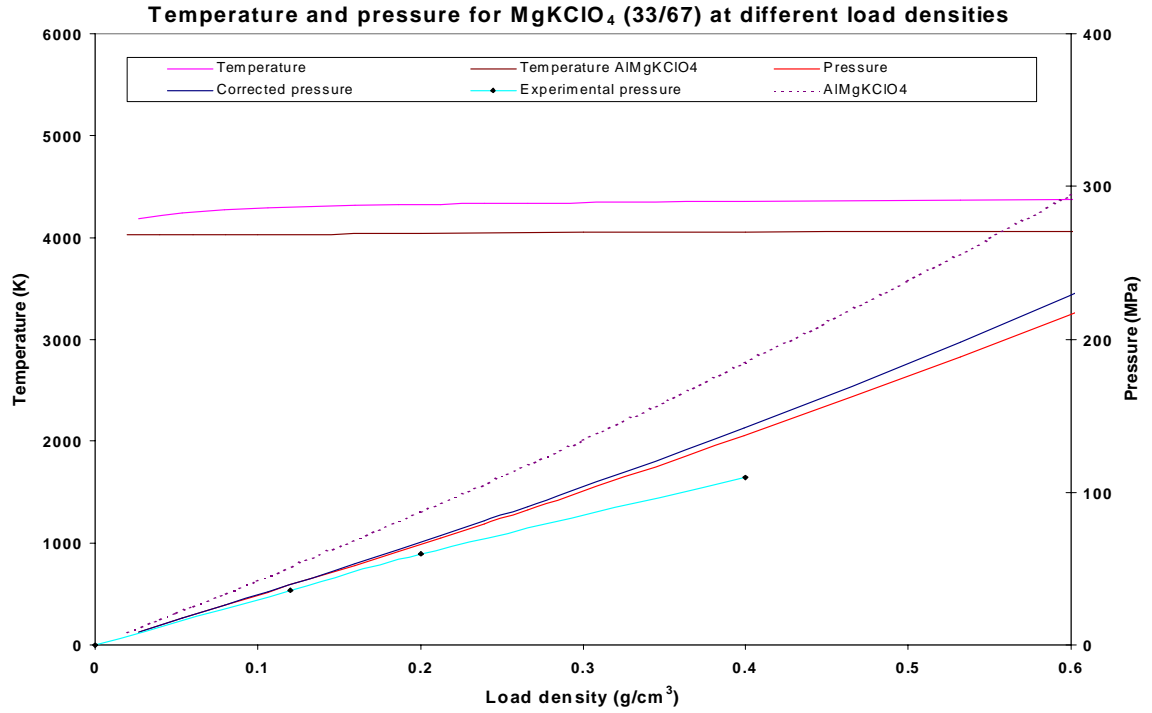


Figure 3.7 Temperature and pressure as function of load density for Mg/KClO₄ (33/67 under different conditions.

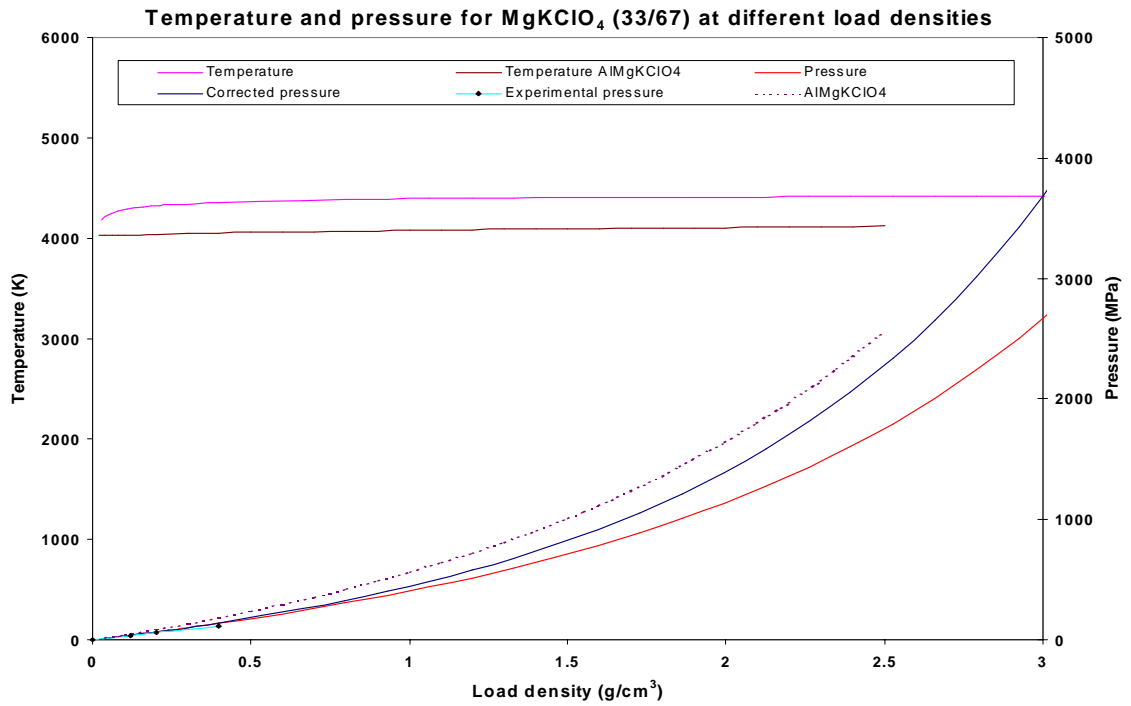


Figure 3.8 Temperature and pressure as function of load density for Mg/KClO₄ (33/67 under different conditions.

$$\rho = \rho_A / [(1 + 0.5 + F) \cdot 0.5]$$

The pressure has been corrected for the co-volume by the following expression:

$$\frac{1}{\left(1 - \frac{\rho}{\rho_{Al}} (0.25 - F \cdot 0.5)\right)}$$

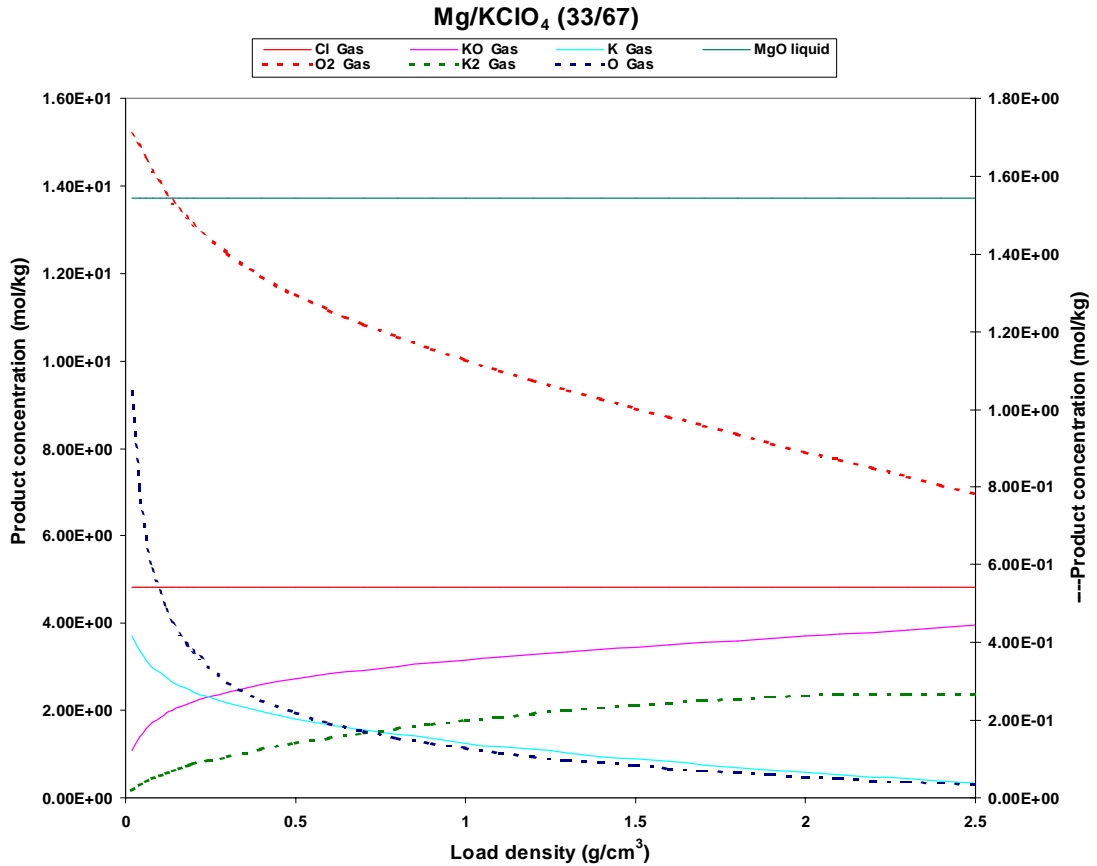


Figure 3.9 Product composition and concentration for Mg/KClO₄ at different load densities ρ .

We observe that a good approximation is achieved by assuming that all aluminium is inert. Based on Cheetah calculations we now reach the following conclusions for the mixture 50 wt.% KClO₄ + 25 wt.% Al + 25 wt.% Mg:

- I. Almost all aluminium is inactive.
- II. The pressure is created by K, Cl and some O₂.
- III. The temperature is close to 4000 K.

3.4 RS-41

Cheetah calculations in Figure 3.10 and 3.11 gives for RS-41 (49 wt.% KClO₄, 49 wt.% Al/Mg alloy, 2 wt.% Calcium Resinate) small deviation compared with the mixture of 50 wt.% KClO₄ + 25 wt.%

Temperature and pressure as function of load density

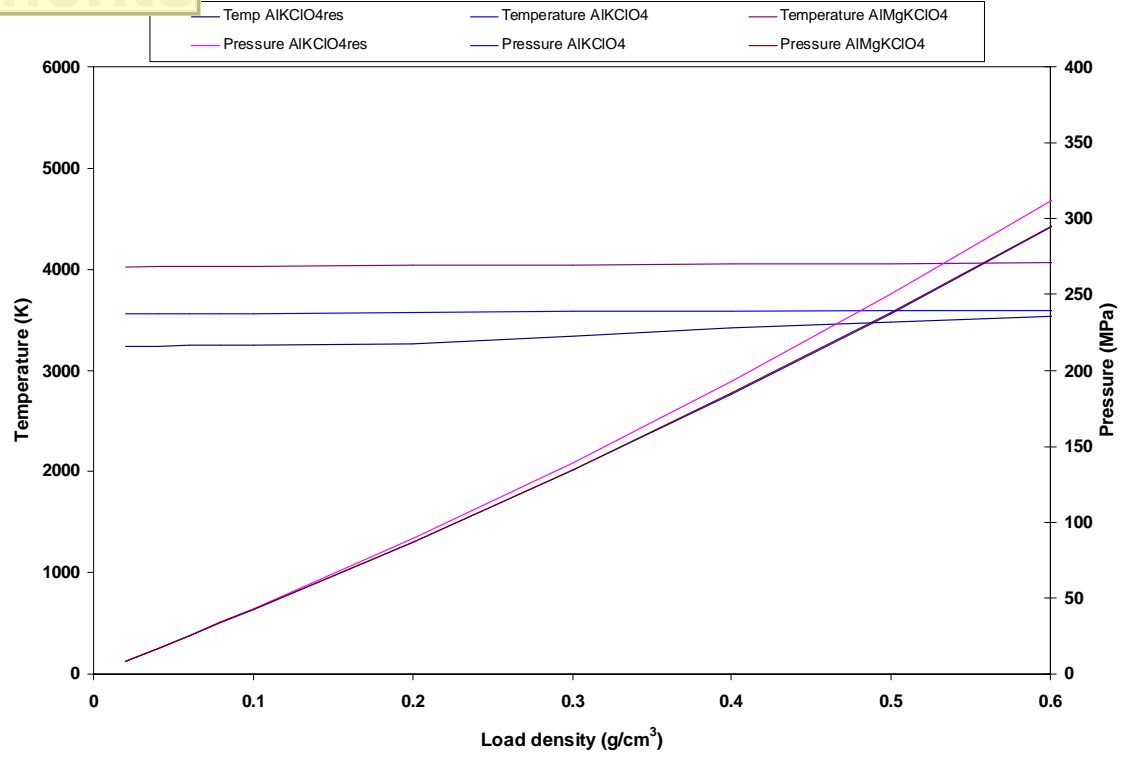


Figure 3.40 Temperature and pressure for equilibrium conditions as function of load density for some compositions calculated by use of Cheetah.

Temperature and pressure as function of load density

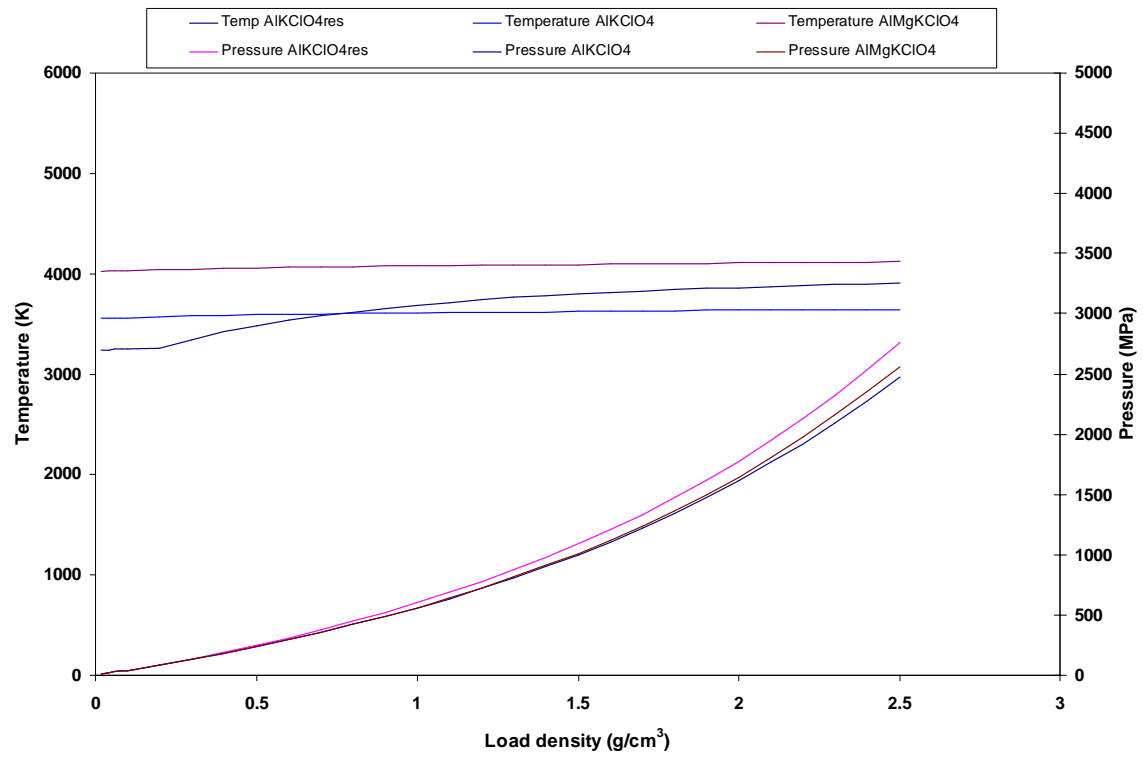


Figure 3.11 Temperature and pressure for equilibrium conditions as function of load density for some compositions calculated by use of Cheetah.

Al + 25 wt% Mg. Both pressure and temperature are approximately the same. This conclusion is in accordance with our experimental measurements at low loading densities. There is no significant difference between RS-41 and the mixture of 50 wt% KClO_4 + 25 wt.% Al + 25 wt% Mg.

4 SUMMARY

The pyrotechnical material RS-41 has been analysed by performing Closed Vessel firings, and by theoretical calculations. The following main conclusions can be drawn:

- I. RS-41 diverges little from the mixtures of 50 wt.% KClO_4 + 25 wt.% Al + 25 wt.% Mg, and 50 wt.% KClO_4 + 50 wt.% Al.
- II. Aluminium contributes little to the pressure build up in RS-41.
- III. The mixture consisting of 50 wt.% KClO_4 and 50 wt.% Mg gives significantly higher pressure than RS-41.

Literature

- (1) Laurence E. Fried, W. Michael Howard, P. Clark Souers: "Cheetah 2.0 User's Manual" UCRL-MA-117541 Rev. 5, Lawrence Livermore National Laboratory. August 20, 1998.

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