

UNDERSTANDING ZINC-SULFUR PROPELLANTS

by Antoon Vyverman



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PART 1

INTRODUCTION

Zinc-sulfur is one of the most popular amateur rocket propellants. The reason for this is that it has many favorable safety and manufacturing characteristics.

In its simplest form, namely as a powder, zinc-sulfur propellants are easy to make, requiring only very commonly available equipment. The same is true for loading the propellant into the rocket chamber. In general, basic safety rules are sufficient and there is normally no need for sophisticated equipment. Even the somewhat more complicated hot cast zinc-sulfur propellant can be manufactured with basic skills and tools.

One disadvantage is that zinc-sulfur suffers from a very low energy content (about 5 times less than potassium nitrate-sugar). As a consequence, the specific impulse is very low compared to other rocket propellants (35s - 55s compared to 110s - 135s for potassium nitrate-sugar). Yet it has a very high density especially when cast ($3.5\text{gr}/\text{cm}^3$ - $4.4\text{gr}/\text{cm}^3$). This makes it possible to attain altitudes in the order of several kilometers, which is still sufficient for most amateurs.

If the propellant is used in powdered form, the rockets' burning times are usually very short. In general, they vary between 0.2s and 0.6s which, given the high accelerations involved, may put measuring equipment in the rocket under severe stress. Thanks to the use of nozzles with very small throats and good chamber coating, it has become possible to extend the burning time to about 3s!

Since sulfur starts melting at 112°C , zinc-sulfur propellants can also be used as cast grains. The density then increases dramatically, and may reach $4.0\text{ gr}/\text{cm}^3$ or even more. A wide variety of thrusts and burning times can be produced.

In the early 1960s the behavior of this propellant was not well understood. Research done by rocket clubs essentially in Belgium (BVRO - now VRO - and J.S-SIVRY) and in the Netherlands (NERO), has solved much of the puzzle. However even today a lot still can to be done.

This book describes our understanding of zinc-sulfur propellants at the end of the second century and refers to many of the experiments executed over a period of about 35 years.

Although only a few names are mentioned in the text, many people have contributed to our present understanding.

A.Vyverman

CHAPTER 1

A BRIEF HISTORY OF ZINC AND SULFUR PROPELLANTS

The history of zinc-sulfur as a propellant goes back to the mid-1940s when rocket amateurs on the US West Coast first used it. Contemporary reports credit the propellant with specific impulses ranging from 20s to 150s, and burning rates ranging from 35 cm/s to 700 cm/s.

In 1960, Brinley published the popular paperback "Rocket Manual for Amateurs". In this book, Brinley described how to design and build a zinc-sulfur rocket. He also mentioned that nearly 50% of the efficiency was lost due to the sublimation of zinc sulfide during expansion in the nozzle. At 1458°K, zinc sulfide solidifies from the gaseous state, and can no longer expand in the nozzle. Apart from the powdered propellant, he described other grain modifications, such as hot and cold cast propellants.

At about the same time, the Swedish engineering group Atlas-Höganäs published a design for a zinc-sulfur rocket.

On the European continent, NERO (Dutch Association for Rocket Research) used zinc-sulfur in the early sixties. The first rockets were tested in flight. When the static test bench was ready, NERO could show for the first time the shape of the thrust-time curves for zinc-sulfur rockets. After several tests, they proved that powdered zinc-sulfur rockets do not burn like ordinary cigarette burners do. Different burning models were postulated to explain the typical thrust time curves, such as the one that assumed that the chamber wall catalyzes burning, so that the propellant burns like a convex cone. Other theories mentioned the possibility of grain deformation during horizontal tests.

Based on the measured thrust curves, Kerkhoven from NERO developed in 1967 a new theory, which he called "*Sublimation theory*". In its simplest form, his conclusion is the following: "The chemical reaction takes about 0,1s. This is the period that the maximum in the thrust-time curve appears. Because ZnS solidifies very easily, the rocket chamber must contain overheated solid ZnS in equilibrium with its vapor. As ZnS leaves the rocket chamber, pressure in the chamber decreases and solid ZnS evaporates, such that the temperature also decreases. Consequently the thrust drops. By the flow through the nozzle the ZnS vapor takes solid ZnS particles with it. Because of the pressure drop in the nozzle, the overheated solid

ZnS evaporates. The gas volume increases." Based on this theory so-called **Zeta nozzles** (see fig.1.2.) were built, giving a higher velocity, and thus a higher efficiency, to the solid particles. Kerkhoven also introduced the variables "*specific length*" and "*specific propellant provision*". He concluded that the specific length,

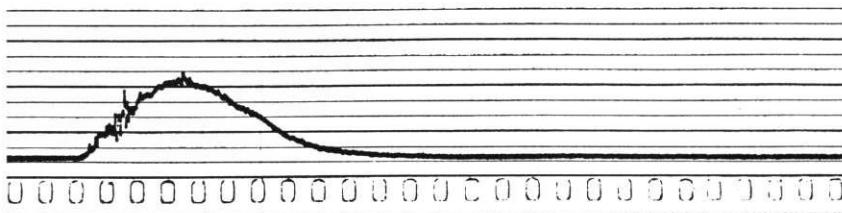


Fig. 16a. Stuwkrachtsdiagram Gamma, 17-1-1965

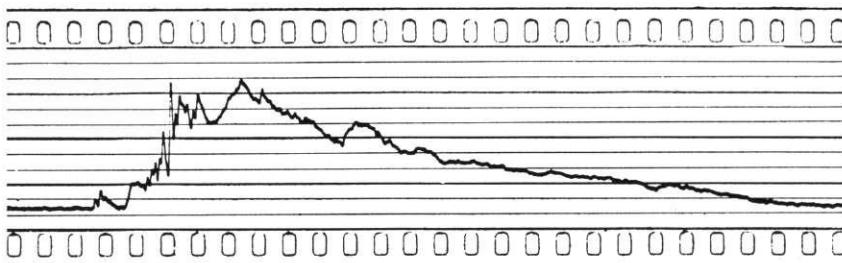


Fig.1.1. Typical zinc-sulfur thrust curves as registered by NERO during the sixties

which is the ratio of the chamber volume to the throat area, and the specific propellant provision, which is the ratio of the initial propellant mass to the throat area, determine the total burning time of the rocket, while the real length of the chamber dominates the time to the top of the thrust-time curve.

In 1967 and 1968, NERO tested the addition of aluminum to the propellant. This resulted in specific impulses situated between 50s and 70s. However, because of higher temperature and pressure, leakage occurred at the front-end and at the nozzle-end of the rocket.

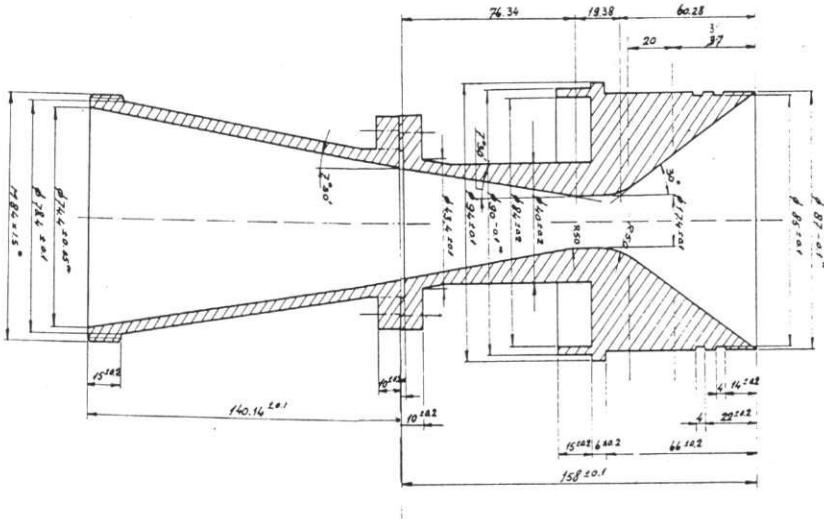


Fig.1.2. Zéta nozzle used in the NERO FALCON 25 motor

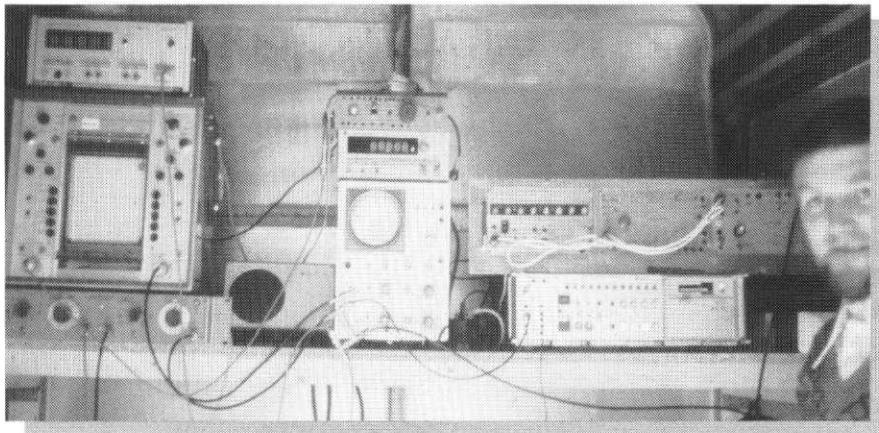


Fig.1.3. Jan Volckaert from BVRO with the combined NERO-BVRO electronic thrust equipment in the early seventies

After this important Zn-S propellant research, NERO concentrated completely on the so-called Co-operation Project. The goal of this project was to launch a two-stage rocket to an altitude of 10 km. The first stage was a zinc-sulfur rocket containing 20 kg of propellant. It was called Swallow motor (see fig.2.1). The

second stage was a Faon, a professional double base motor built in France. Different launchings took place in La Courtine (France) and Oldebroek (Netherlands). Although the ultimate goal was never reached, the zinc-sulfur rocket always performed well.

We had to wait until 1975 for the next important step in the zinc-sulfur propellant research. The development of static test equipment by Jan Volckaert, made it possible for the BVRO (Belgian Rocket Research Association) to verify the sublimation theory. After a series of tests, some of the theory's basic ideas could be confirmed. It could be shown that the total burning time is indeed determined by the specific propellant provision (see fig.3.6). However,

the influence of the chamber length on the time to the top of the thrust curve, could not be confirmed (see figure 3.3). The introduction of the notion "**Penetration phase**" was introduced to explain this phenomenon, and the theory about the reaction phase was revised. It was accepted that the hot gasses, which have the ability to penetrate easily through the powdered grain, ignited all the propellant mass in a very short time. Relying on these ideas, we found that the thrust-curves for powdered zinc-sulfur rockets, when represented in a diagram with on one hand the thrust divided by the throat area (F/At), on the other hand the real time divided by the total burning time (t/t_{tot}), are all very similar (see fig. 2.7)



Fig.1.4: Alain Peerts from BVRO in the early Seventies with an ABIM rocket.

The chemical reaction takes more time than 0.1s, but the increasing thrust is quickly equilibrated by the thrust decreasing effect caused by the exhaust flow of the solid and gaseous reaction products, ZnS and Zn . The introduction of these ideas made it

possible to explain what happens when, for instance, the diaphragm, which is placed in the nozzle to create pressure building up at ignition, is weak or strong. Several rockets were built with high values of the specific propellant provision. These rockets showed burning times of more than 1.5s. The tests convinced us that it was possible to ignite the propellant from the aft-end of the motor instead of the nozzle-end. NERO was the first to apply this idea successfully.

BVRO also conducted some experiments with cast zinc-sulfur from the melt, called *hot cast zinc-sulfur*. Very good results were obtained with 1% of aluminum added to the stoichiometric mixture. Burning times of 2 to 3 seconds and impulses of 49s were registered.

In 1977, a thermodynamic study of the propellant was made as a first attempt to model the behavior of this type of rockets. It became the basis for a much greater insight into the phenomena that occur in these rockets.

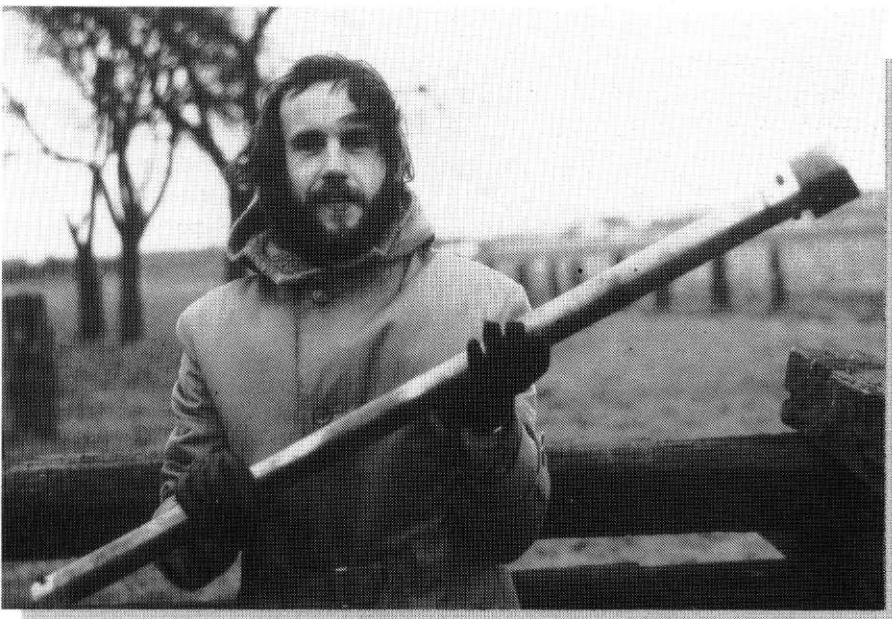


Fig. 1.5. A. Vyverman with the DX-21 rocket in 1971

At about the same time, another Belgian group, J.S. of SIVRY was doing important work. This rocket group developed the SIVRY X rocket, propelled by hot cast zinc-sulfur. The rocket was used with much success for several launchings.

When using a liner on the surface of the propellant, J.S.SIVRY could realize an almost flat thrust diagram (see fig.4.2.). They did much research into the propellant grain and its structure. Also the Danish group DARK performed some interesting

experiments with hot cast zinc-sulfur. From these tests, we concluded that the burning rate of hot cast Zn/S 3/1 propellants is around 10 cm/s.

Back to the Netherlands. In 1987, NERO manufactured the largest known zinc-sulfur rocket, called ALBATROS. With a propellant mass of 45 kg, the rocket developed a thrust of more than 20000 N. NERO also measured pressures in the rocket chamber, in the nozzle throat and in closed reaction chambers. These measurements were of very high interest. Dirk Van Gelderen from NERO found that powdered zinc-sulfur rockets behave differently in flight than on the ground. Indeed based on NERO's measurements, we could show that the thrust during flight could be 3 to 4 times larger than the thrust during ground tests, with corresponding smaller duration (see figure 3.18).

Over the last few years, BVRO (now VRO) has again shown increasing interest in this propellant. Several hot cast zinc-sulfur propellants, with up to 10% of aluminum, were tested in an attempt to increase the specific impulse to higher values



Fig.1.6. ZAS5-2 with aluminized Zn/S

and at the same time to produce controlled curves. The first results gave specific impulses up to 56s, which is on the high side for zinc-sulfur propellants but lower than expected. The thrust curves were still irregular. This probably stems from the fact that the propellant, at low sulfur content, is a very good heat conductor (high zinc and aluminum content) and that there may be different burning modes depending upon the conditions in the rocket chamber and its past history (heating the grain). With a sulfur content over 25% the thrust curves conform with regular burning. Improved propellant preparation methods increased the propellant density from 3.4 gr/cm³ to about 3.8 g/cm³.

In an attempt to better understand the behavior in the rocket nozzle, a model was developed based on thermodynamic calculations. We were able to come up with calculated performances extremely close to the measured ones. However a lot is still to be done to come to a complete explanation of this propellant.

Although much has been realized over the past 35 years, not everything is completely understood, and there still is scope for intensive testing and new ideas.

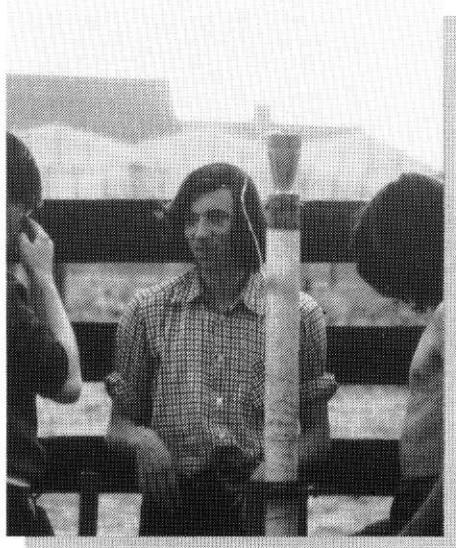


Figure 1.7. Chris Steyaert with the ABIM rocket motor in 1971

PART 2

A GENERAL DESCRIPTION OF ZINC AND SULPHUR ROCKETS

CHAPTER 2: INTRODUCTION

As an amateur rocket propellant, the mixture of Zn and S is mostly used under two forms: as a powder, which is the simplest form, or heated till liquefaction of the sulfur. In the latter case, called *hot cast*, it becomes a hard, strong, heavy grain. The two propellants behave quite differently. In the case of the powder, the reaction between zinc and sulfur is very violent and the reaction time is very short. When hot cast zinc and sulfur is used, it produces a large variety of combustion times and thrust-time curves. Other modifications of the propellant include a powder compressed to very high pressures and cold cast with the use of solvents.

Although other mixtures have been tested, the most frequently used compositions are two parts of zinc to one part of sulfur by weight (2/1) and three parts of zinc to one part of sulfur (3/1).

The first composition (2/1) is *stoichiometric*. This means that when the reaction is completed only zinc sulfide (ZnS) is left. The second composition has an excess of zinc. After reaction all sulfur is consumed to ZnS. The excess of zinc undergoes no chemical reaction.

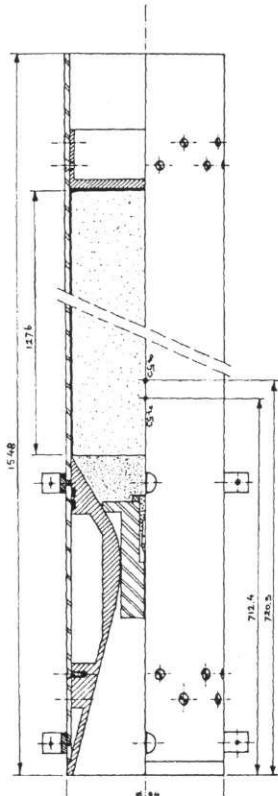
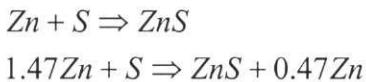


Figure 2.1. NERO Swallow rocket

Since any excess of zinc in the mixture is to be considered an inert component, the stoichiometric composition is much more violent and releases more heat per unit of propellant mass. Consequently reaction temperatures and pressures will be higher when the propellant is used in powder form, resulting in shorter reaction times, higher risks of leakage and corrosion of the nozzle throat. The specific impulse of the 3/1 mixture is greater than that of the stoichiometric mixture. In practice it is advisable to use the 3/1 mixture (lower temperature, less corrosion, higher specific impulse and higher propellant density) or even higher ratios of zinc to sulfur. With the 2/1 ratio, one can expect a specific impulse in the range of 30s to 35s, while the specific impulse of 3/1 mixtures will generally range from 38s to 50s. Because 3/1 has a higher content of the heavy zinc, its density will also be larger: 2.8 g/cm³ - 3.1 g/cm³ for powders, 3.8 g/cm³ - 4.2 g/cm³ for hot cast grains; compared to 2.2 g/cm³ - 2.4 g/cm³ for 2/1 powders and 3.6 g/cm³ - 3.8 g/cm³ for hot cast grains. The theoretical density of 3/1 is 4.35 g/cm³ compared to 3.85 g/cm³ for 2/1 mixtures.

The motor of a zinc-sulfur rocket is the same as for other rockets (fig.2.1). It consists of a nozzle with divergent and convergent sections, and a cylindrical chamber.

The most common means to induce the reaction is an electrical igniter fixed on a diaphragm. This diaphragm is fixed on the nozzle to ensure sufficient initial pressure to prevent ignition failures.

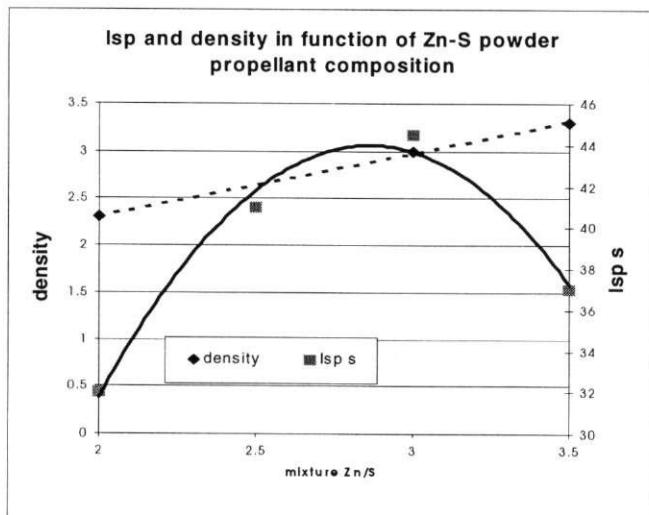


Figure 2.2. Propellant composition versus Isp and density

CHAPTER 3

POWDERED ZINC-SULFUR PROPELLANTS

Once the two components are mixed, the powdered propellant is poured gradually into the rocket chamber, and gently pressed to increase its density. Depending upon several parameters such as propellant composition, particle size, propellant mass and nozzle size, the thrust-time curve generally has the shape depicted in figures 1.1 and 3.1.

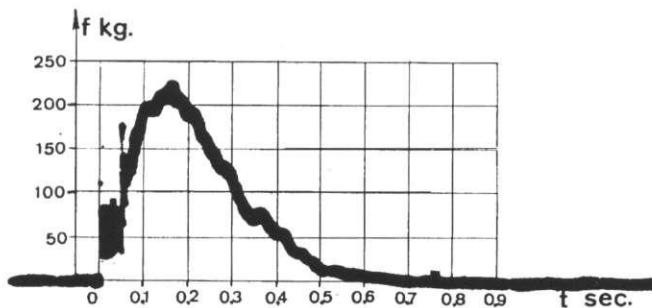


Figure 3.1. Thrust curve of a 2/1 powder rocket (BVRO)

The reasons for this particular behavior have been the subject of much research.

Before 1967, it was believed that the fuel in powdered zinc-sulfur rockets burns in parallel layers. At that time, many amateurs reported very high burning rates. Kerkhoven from NERO was the first to recognize that this was virtually impossible. He developed a theory called "***The Sublimation Theory***" which explains that the behavior of zinc-sulfur rockets is totally different from cigarette burning rockets. Several of his ideas could later be proven in tests performed by BVRO and NERO. Based on the new findings, the sublimation theory was revised and extended. An attempt was also made to give zinc-sulfur rocket research a thermodynamic background. Far from being complete, the thermodynamic approach opened a new perspective on the behavior of these rockets.

3.1. First ideas about the burning mechanism of powdered zinc-sulfur rockets

Before 1967, it was generally accepted that zinc-sulfur rockets are cigarette burners. Brinley (ref.13) mentioned burning rates of 90 inches a second, as a result of tests done by the Army Artillery and Missile School at Ft. Sill Oklahoma.

The NERO was among the first to register the thrust-time curves of zinc-sulfur rockets. In all experiments the rockets delivered a curve far different from what could be expected from a cigarette burner.

One theory from that time claimed that the propellant burns like a cone with the burning catalyzed by the wall. Another possibility considered was that the powder comes loose and is shifted down by gravity. Test in vertical position however produced similar thrust curves.

It was clear that zinc and sulfur rockets do not burn like other rockets do!

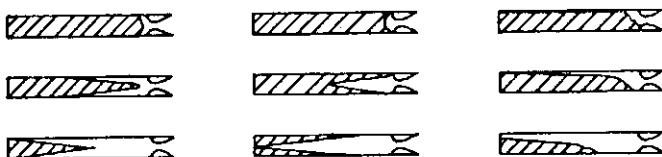


Figure 3.2. Early theories about the burning mechanism of powdered zinc-sulfur propellants

3.2. The impact of a loose powder on the reaction phenomena

Different people already observed, for instance when leakage occurred, that the flames reach the end of the rocket chamber in a time that is much smaller than the rocket's total burning time. Kerkhoven explained this behavior.

The main difference between powdered zinc-sulfur, and ordinary propellants, is simply that we have here a relatively loose powder. About 30% to 40% of the rocket chamber is filled with air. When pressure rises, the hot gases are pressed between the particles and ignite them. Kerkhoven suggested further that the other side of the combustion chamber is reached after about 0.1 seconds. According to Kerkhoven's explanation the time needed to reach the end of the combustion chamber is the same as the time needed for the thrust to reach the top of the curve. Checking this idea by plotting the time to the top of the curve versus the real length of the rocket, however

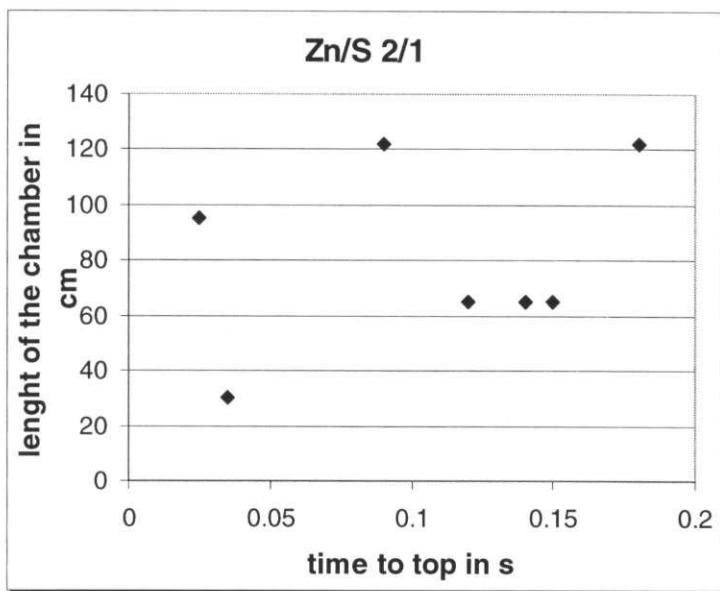


Figure 3.3. Time to the top of the thrust curves versus the length of the combustion chamber

did not reveal any significant correlation (fig.3.3.).

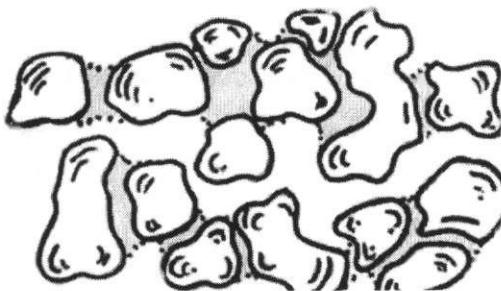


Figure 3.4. Channel formation in powdered zinc-sulfur propellants

This means that the length of the rocket chamber does not at first instance determine the time to the top of the thrust curve. We believe that the time for the chemical reaction and the time to reach the end of the combustion chamber are different and

that both are to be considered separate processes. Before ignition, the propellant is a very porous mass, provided with a system of channels. The air is not enclosed in isolated cells, but is interconnected by the channels (figure 3.4.).

It is clear that at ignition hot gases can easily penetrate the channels, to reach the other end. (figure 3.5.)

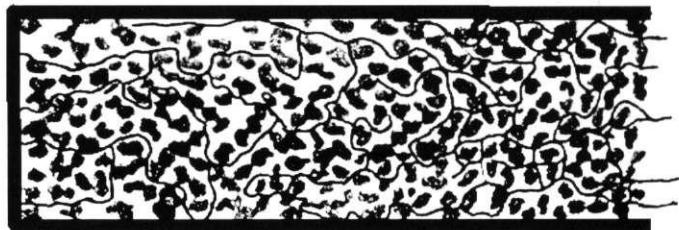


Figure 3.5. Gas penetration through the channels

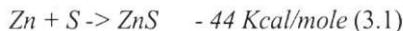
In a closed system, which is the case when the igniter-diaphragm is still in the rocket, the propagation by pressure difference will be very fast - much faster than the chemical reaction. It is clear that when the diaphragm is loose, and the propellant densities high, there will be ignition problems. *A certain time at high pressure and the ability to penetrate are necessary for the hot gases to ignite the total propellant mass.* When the burst pressure of the diaphragm is too low, there won't be enough penetration and hence ignition will fail. Much experimental evidence of this was gathered over the years.

3.3. The sublimation theory according to Kerkhoven

We shall summarize what he wrote in 1967.

"Zinc sulphide is a solid at ordinary temperatures. At elevated temperatures a vapor pressure is created which increases to 1 bar at 1185°C. ZnS will then sublime without melting. If the temperature goes still higher, the vapor pressure will increase very rapidly

When a mixture of zinc and sulfur is ignited, the following reaction will occur:



(the negative sign denotes release of heat, i.e. exothermic)

The heat of reaction (43 to 48 kcal/mole) is sufficient to heat ZnS far above its sublimation temperature. The vapor pressure must then be in the range of 150 bar. In the combustion chamber, the larger part of ZnS will, because of the high pressure, be in the solid state. If this were not be the case, the rocket would explode. In practice, the mixture of the unreacted powder has a density of 2,3 to 2,6. If we take 2,3, then according to Boyles law ($PV = nRT$) the pressure in the chamber would have risen to 2840 bar at 1185°C. At 1400°C (what Brinley thought was the flame temperature) the pressure would be 3500 bar! In reality, according to the thrust developed, the pressure must be in the neighborhood of 100 bar.

The chemical reaction is over in about 0,1 seconds. This is the period the thrust has to increase to its maximum value. The temperature in the chamber is also at its maximum and of all the ZnS, only about 30% has left the rocket. In the rocket itself, solid ZnS is in equilibrium with its gas. As more zinc sulfide vapor (and solid) flows through the nozzle, ZnS vaporizes.

Since this transformation consumes the sublimation heat, temperature and pressure will decrease. Consequently the thrust drops, as can be seen in each thrust-time curve.

When the temperature drops to 1185°C, the vapor pressure is 1 bar, and the flow through the nozzle stops. Any remaining ZnS will later be found as residue on the wall."

3.4. Specific length and specific propellant provision.

Since according to this theory, the use of the ratio of propellant burning area to throat has no sense for this type of rockets, Kerkhoven developed two new parameters to specify the rocket performances

$$\text{"specific length"} \quad L_{sp} = \frac{V_c}{A_t} \quad (3.2)$$

$$\text{"specific propellant provision"} \quad B_{sp} = \frac{M_b}{A_t} \quad (3.3)$$

In these formulas, V_c is the volume of the reaction chamber, M_b the initial propellant mass, and A_t the nozzle throat area.

These two parameters, Kerkhoven expected, would determine the *residence time* of ZnS in the rocket motor, or in other words, the working time. As already mentioned, he also thought the real length of the rocket determined the time to the top of the curve. But as we have seen this is not the case. At that time, there was not enough

experimental material to confirm his thoughts.

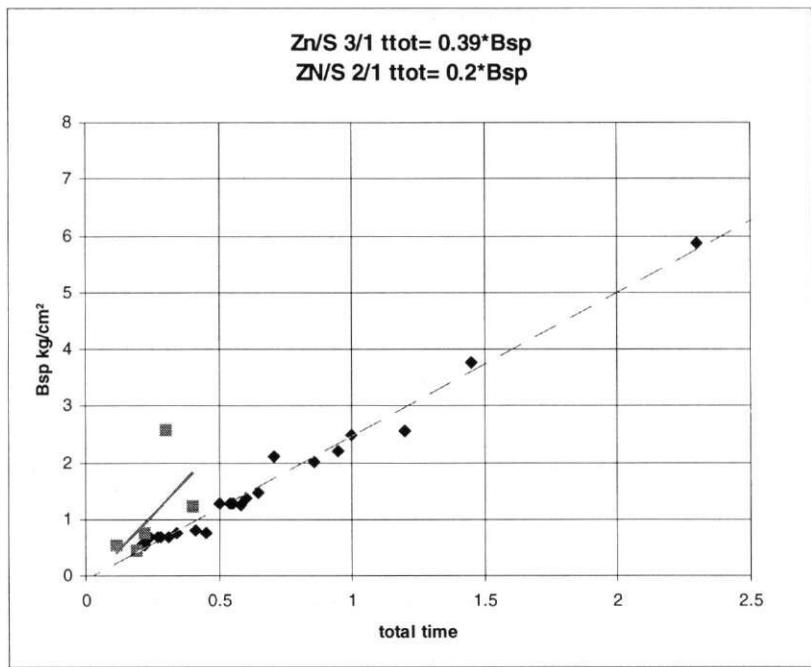


Figure 3.6. Relation between Bsp and total burning time

Years later its validity was tested. This was essentially done by the BVRO in 1975, where at that time a number of tests were performed with different Bsp's. When the total reaction time was plotted against Bsp the following correlation was found (fig.3.6.):

$$t_{tot} = \alpha B_{sp} \quad (3.4)$$

With $\alpha = 0.39$ for Zn/S 3/1 and 0.20 for Zn/S 2/1 when B_{sp} is expressed in kg/cm^2 .

On the other hand, and as also already mentioned, no correlation was found between the real length of the rocket and the time to the top of the curves. However, when the time to the top was plotted against Bsp, we found a very good correlation. This was the key to a different explanation of the chemical reaction:

The unreacted propellant powder occupies about 60%- 70% of the available volume of the reaction chamber. Under these circumstances about 40%-30% of the total chamber volume is occupied by air. The air is not captured in isolated cells but is interconnected in a system of canals. It is obvious that at ignition hot combustion products can easily penetrate the packed powder and cause the ignition of all available particle surfaces. This is the *penetration phase*. During the penetration phase the reaction between Zn and S starts to create ZnS.

Since only very small particles are involved, the total surface is very large and the reaction rates consequently high. As the reaction goes on, the rate decreases with decreasing availability of sulfur and zinc.

In a rocket motor, the amount of material expelled through the nozzle is a function of the chamber pressure and the nozzle throat area. This means that two opposite mechanisms determine the pressure-time curve. The chemical reaction tends to increase the pressure while the discharge through the nozzle tends to lower the pressure. This generates 3 different phases in the pressure time curves.

-"progressive phase"

At the beginning of the reaction, the rate of ZnS production is very high but pressure is low, such that more material is generated than expelled. The pressure rises.

-"steady state"

As the pressure rises, an increasing amount of material will be exhausted, while the consumption of the available zinc and sulfur slows down the reaction rate. The pressure-time curve will flatten and reach a point where generation equals discharge. The rocket is in steady state and has reached its highest thrust and pressure.

-"digressive phase"

Since the combustion rate decreases steadily, and more material is expelled, a digressive phase must occur.

Based on these mechanisms one can easily see that the throat area has a significant influence on the total working time. If this area is large the top of the curve will be reached sooner than when it is small, since more material will be discharged and for the same reason the digressive phase will also become shorter. *This means that the nozzle throat area can regulate the total burning time*. It is clear that the nozzle throat area also affects the thrust. In fact the maximum thrust is linear with the throat area (see figure 3.7.), while the total burning time is linear with the "specific propellant provision" Bsp.

The occasionally strong data deviation from the straight line in figure 3.7., is due to the influence of other parameters on the relation, such as:

- propellant density (the higher the density the more difficult the penetration of hot gases and thus the lower the thrust),

- the length of the reaction chamber (the longer the reaction chamber the more time it takes to ignite all the powder and again the lower the thrust),
- and also the Isp which varies between 38s and 50s for 3/1 powders.
- The burst pressure of the diaphragm and the amount of ignition powder also influence maximum thrust.

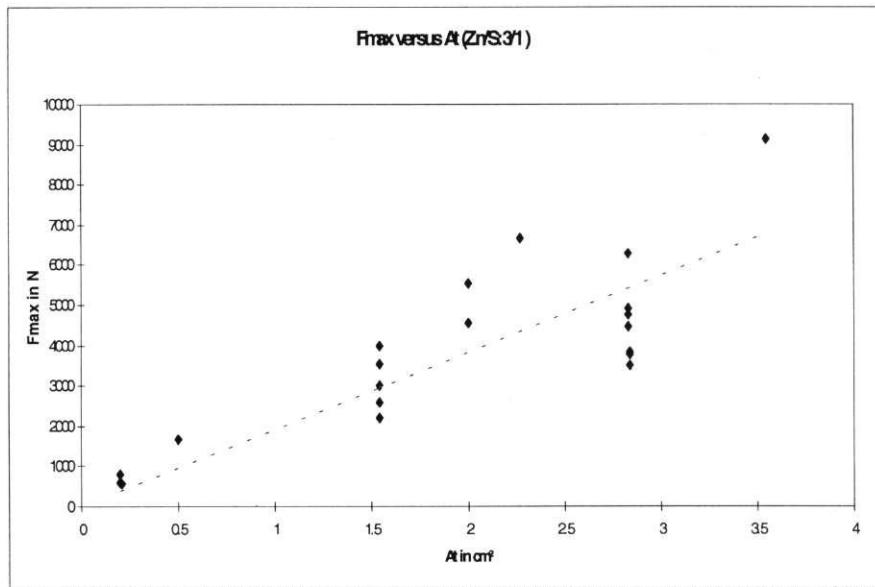


Figure 3.7. Relation between maximum thrust and throat area

Since Bsp affects the burning time and At the thrust, one can plot the thrusts in a F/At against t/Bsp*α curve. (see fig. 3.8):

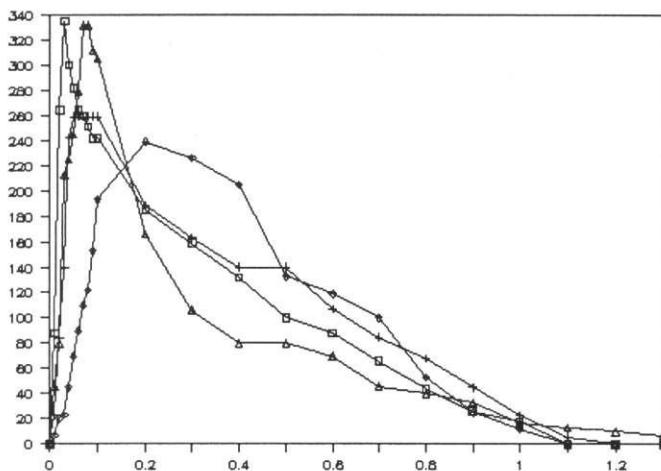


Fig.3.8. Several Zn/S 3/1 thrust curves in a F/At vs $t/Bsp.\alpha$ diagram

3.5. The chemical reaction.

We have already explained that at ignition, a penetration takes place first. At penetration, the reaction between zinc and sulfur starts. When the gases pass through the channels, sulfur is heated to very reactive vapor that can attack the free surface of the zinc particles creating gaseous zinc sulfide.

The heat produced by this reaction is used to transform the solid zinc and sulfur into the gaseous state. Since sulfur is easier to evaporate than zinc, this will occur first. When the gas flows through the channels, it condenses on the cold solid particles. The heat created by this transformation again creates gaseous sulfur, which in turn attacks solid zinc particles ...

This figure also explains why under certain circumstances, mostly when there is no overdose of zinc, the rocket wall is corroded by sulfur vapor creating leakage (see figure 3.10).

Since the reaction between zinc and sulfur (which lasts longer than the time to the top) tries to increase the pressure, while the flow of mass through the nozzle, tries to decrease the pressure, the combination of both phenomena will determine the time to the top. This depends strongly on the burst pressure of the diaphragm.

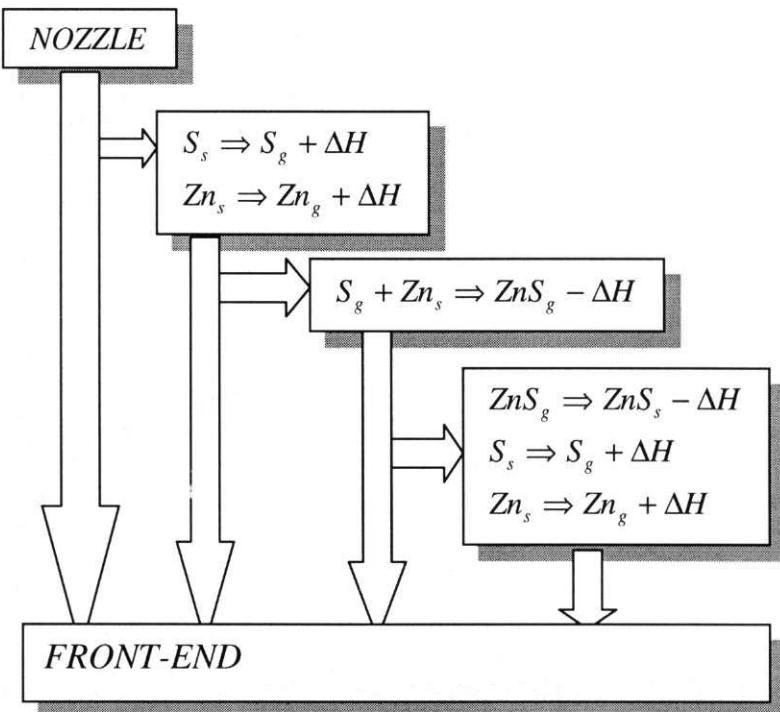


Fig. 3.9. Reactions occurring during the penetration phase

It is clear that as the reaction continues, the zinc and sulfur become exhausted. Consequently the rate of reaction decreases. Total conversion will only be reached asymptotically. The pressure curve would be likewise.

The tendency of the pressure to drop because of the flow through the nozzle, is a function of the pressure in the chamber. As pressure increases, a bigger mass flow will pass the throat. It is obvious that a given mass flow will have only a small impact on the pressure drop when the chamber is very large and contains much zinc sulfide (only a small part of the mass-content of the chamber is then exhausted). Under these circumstances it will take long to empty the chamber. From this it follows that there must be a relation between the pressure drop and the volume of the chamber.

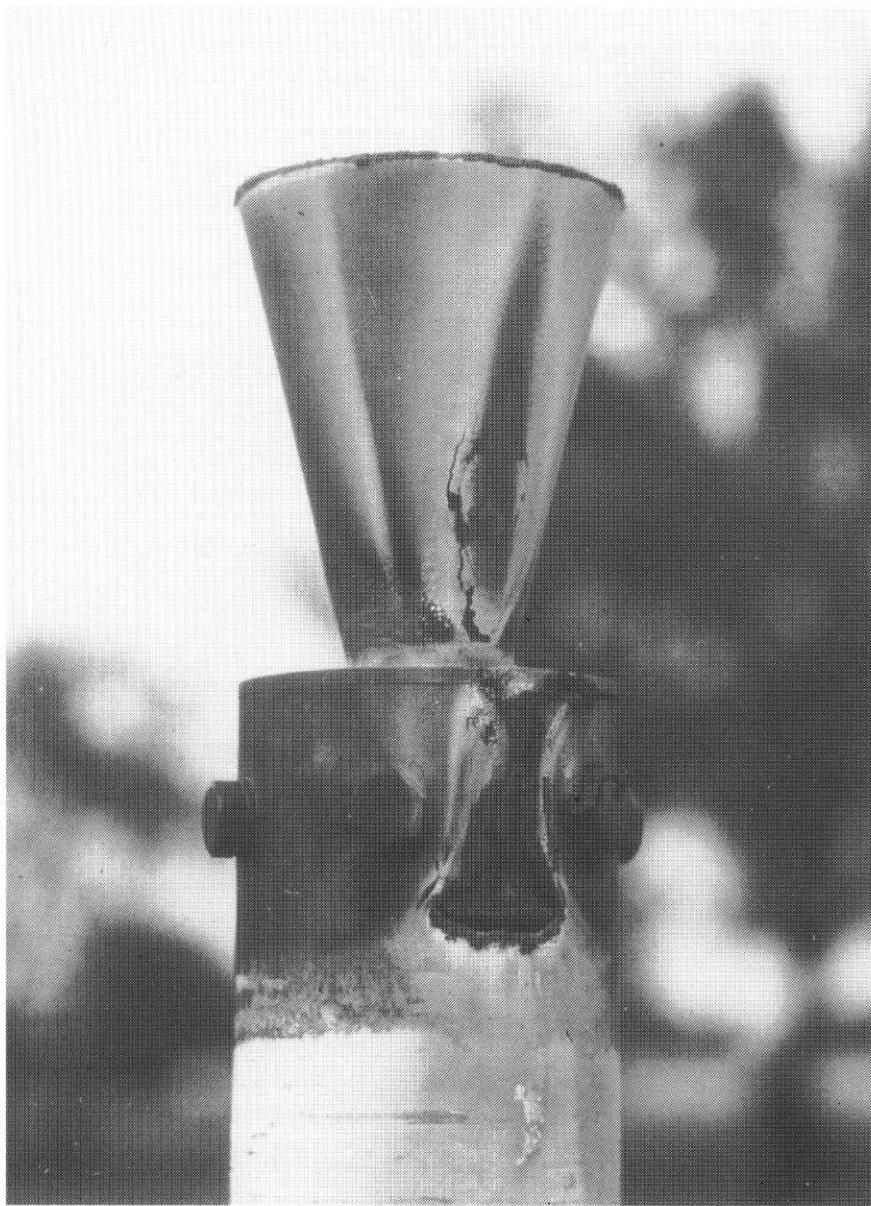


Figure 3.10. Leakage in a Zn/S 2/1 rocket (BVRO)

Instead of taking the volume, one can also take the initial mass content (the difference being the density). In the diagrams in figure 3.8, we plot the thrust curves for rockets whose total propellant mass ranges from less than 1 kg to up to 45 kg! The measured curve can, however, also be influenced by the burst pressure of the diaphragm or by the density of the propellant. In the latter case, very high-density powders may behave somewhat between powders and cast propellants, because of a limited penetration. This would shift the top of the curve to the right.

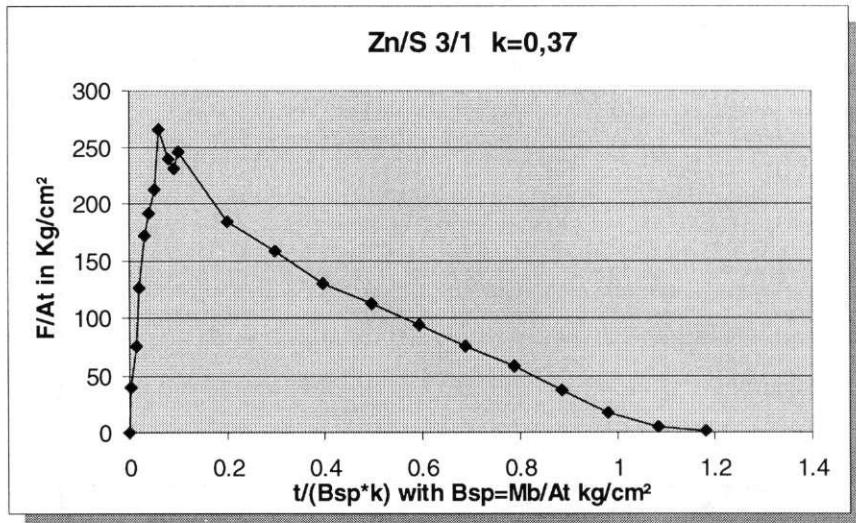


Figure 3.11. Generalized thrust curve for 3/1 rockets

In figure 3.11, we put all 4 curves from 3.8 in one general curve. Note that the surface under this type of diagram (F/At against $t/Bsp\alpha$) is nothing else than u_e/α !

In the case of zinc-sulfur propellants, the throat diameter can almost always be altered without danger of explosion, this in contrast to more classical propellants. Zinc-sulfur propellants behave this way because the reaction products, gaseous ZnS and gaseous Zn, are not low boiling products. ZnS sublimates only at very high temperatures and requires much energy to heat up. This is also the case for zinc. *The reaction heat is insufficient to bring all zinc and zinc sulfide into the gaseous state.* As a consequence the larger part of ZnS and Zn will be solid or liquid in equilibrium with the gas. The sublimation heat of ZnS is about 60% of the reaction heat. This means that the transition from one phase to the other will largely influence the equilibrium temperature and pressure. When ZnS solidifies, heat is released (heat generation) and the temperature will rise. On the other hand the temperature will decrease when ZnS is evaporating (heat consumption).

When the reaction starts for a stoichiometric mixture producing only ZnS, gaseous ZnS is created until the pressure rises to a point where equilibrium is achieved and solid ZnS is formed. Heat is released and consequently the temperature and the pressure will increase. As time goes on more material is discharged through the nozzle, consequently less ZnS is left in the motor and more room will be available for ZnS to evaporate lowering pressure and temperature in the rocket chamber.

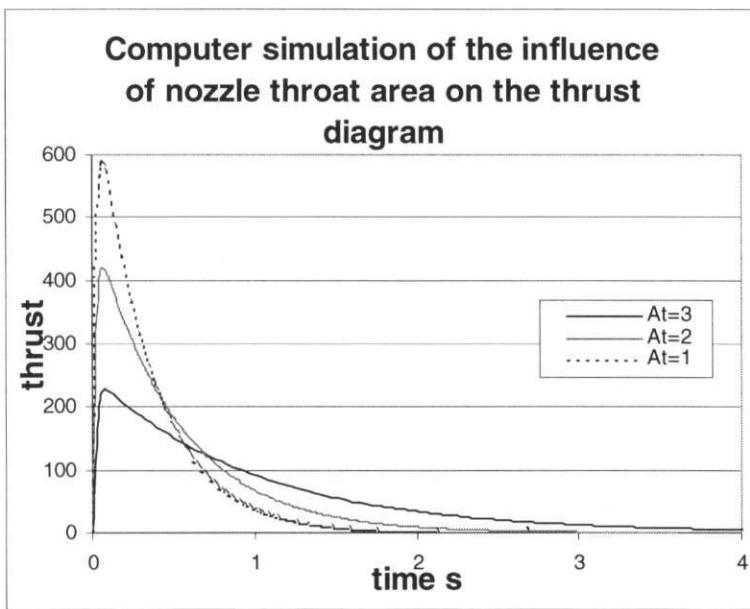


Figure 3.12. Influence of the throat area on the thrust-time curves.

Calculations show that in the combustion chamber, the amount of solid ZnS at maximum thrust must be more than 95%, while the temperature rises to 2500°K-3500°K, depending on the composition.

It is clear that this situation must have a significant influence on the behavior in the nozzle.

Following mechanisms are involved:

- ✓ the gases (both ZnS and Zn) gain speed by expansion thereby lowering their temperature.
- ✓ a temperature difference between the solids and gases will occur since solids do not expand

- ✓ because of the pressure drop, part of the condensed particles will evaporate
- ✓ because of the temperature difference there will be a heat flux from the hot solids to the expanding gas.
- ✓ solids gain speed from drag exerted by the flowing gas.
- ✓ since solids cannot expand, they tend to go straight while gasses fill the entire space of the nozzle

Consequently, the solids will have lower speed and higher temperatures than the gases at any point in the nozzle. This is shown in figure 3.12.

Only low impulses can be achieved because a large part of the available energy is still enclosed in the hot solid particles and is not converted to kinetic energy.

How can impulses be increased? From a purely energy point of view, one can calculate what the specific impulse would be for a stoichiometric mixture when, at the end of the nozzle, all the ZnS is in the gaseous state or in the solid state at the sublimation temperature of 1458°K at 1 bar (pressure at the end of the nozzle). This calculation is based on the difference between the heat of reaction (H_R) and the enthalpy (H_e) content at the end of the nozzle:

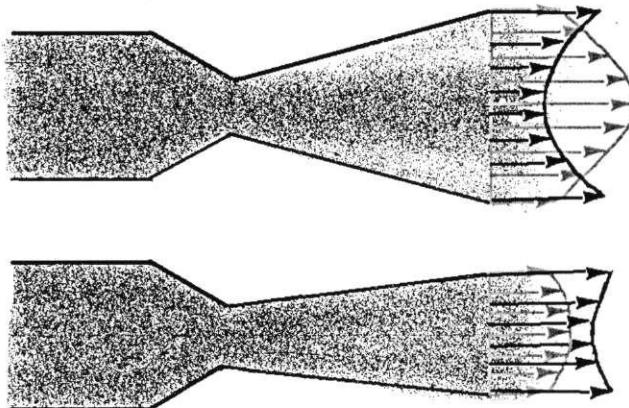


Figure 3.12. Expected speed (blue) and temperature (green) distribution in classical (15° outlet) and zeta-type (7.5°) type nozzles

$$ue = \sqrt{2(H_R - H_e)} \quad (3.5)$$

In the first case (only gas at the end of the nozzle $H_e = 44847$ cal/mole) the exhaust velocity would be about 0 m/s (with $H_R = 45000$ cal/mole). We believe however that a reaction heat of even 45000 cal/mole is not reached in the motor and that 38500 cal/mole is more realistic. This means that the reaction heat is insufficient to heat all ZnS to the gaseous phase. In the second case (only solids at the end) the

exhaust velocity would be around 1400 m/s! The impulse would be larger in the second case because the sublimation heat, which is otherwise contained in the gas, is converted into kinetic energy. Of course, in the second case gas must expand in the nozzle, but should become solid at the end of the nozzle. It is clear that this situation is only theoretical and cannot be achieved in reality.

To improve the specific impulse, one should:

- ✓ First of all ***insulate the inner chamber*** wall properly to prevent heat loss to the wall.
- ✓ Secondly all attempts to come up with a very high, low-temperature, condensed fraction at the end of the nozzle will benefit the specific impulse. Improving the heat transfer from the solids to the gas is one way to do this. ***Therefore long nozzles with basically small outlet angles*** are beneficial. The so-called Zéta nozzle (see fig. 1.2.) with an outlet angle of 7.5° indeed delivers better results.

3.6. Chamber pressure and thrust coefficient

NERO measured the pressure at several locations in a number of zinc-sulfur motors as well as in closed chambers. Figure 3.13. depicts some of the results.

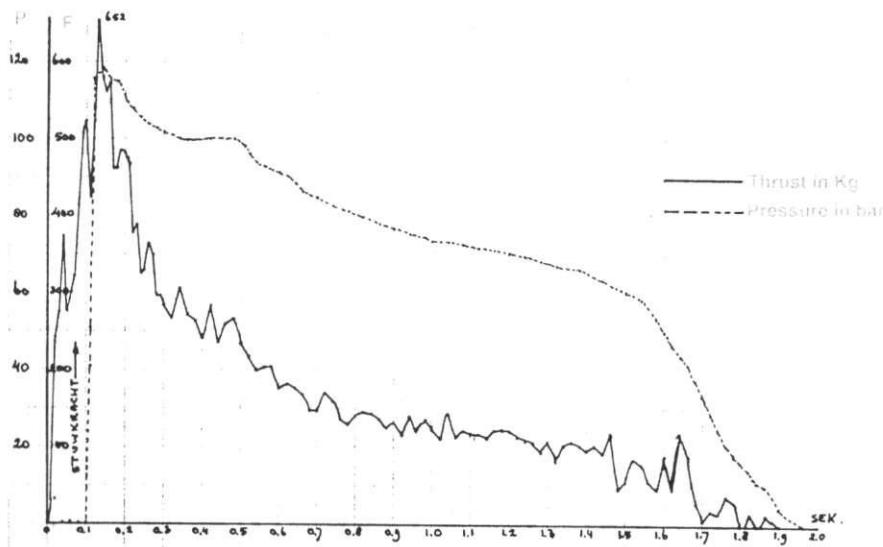


Figure 3.13. Chamber pressure measurements in NERO rocket E34

These measurements show that a peak pressure of 120 to 140 bar occurs in the initial phase of the burning. They also illustrate that there is only a very slight

pressure difference between the front end and the nozzle end. Moreover, the measurements permitted calculation of the thrust coefficient as a function of the pressure. This is represented in figure 3.14. The results are remarkably within the range of Cf-values for double base and composite propellant rockets. It should be indicated here that the thrust coefficient at lower pressures is based on an expansion in the rocket chamber already having taken place, not only lowering the pressure but also the temperature. *This means that these Cf-values cannot as such be used for hot cast propellants!*

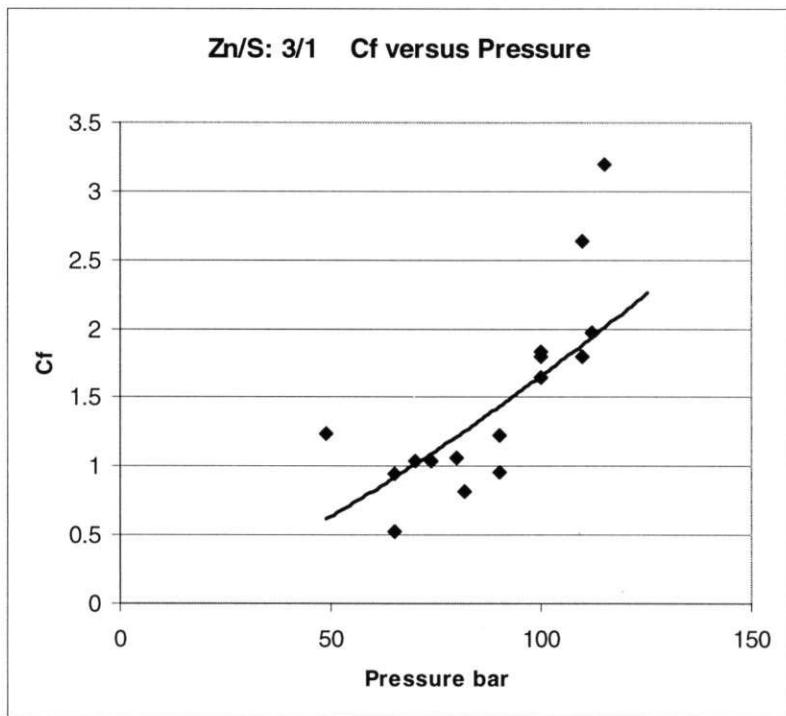


Figure 3.14. Cf versus chamber pressure as derived from several NERO measurements

3.7. Ignition of zinc-sulfur rockets

Zinc-sulfur powder propellants can only be successfully ignited when a critical penetration of the hot gases through the propellant is assured. Ignition will thus be more difficult with increased propellant density.

Another factor that influences the success of ignition, is propellant composition. The lower the reaction heat, the lower the vapor temperature and consequently the more difficult the ignition.

Particle size will have a great influence on ignition, since large particles react less violently than do small particles. This is due to the much smaller surface area of large particles compared to small ones.

Depending upon the location, several types of ignition can be considered.

- nozzle-end ignition
- front-end ignition
- central tube ignition

3.7.1. Nozzle-end ignition

This type of ignition is the most common and oldest method to ignite a zinc-sulfur rocket motor. The ignition system consists of an igniter and a diaphragm located at the nozzle. The diaphragm burst pressure must be high to assure adequate ignition. Figure 3.15 shows different designs. In the drawing on the left, a plug (mostly wood) is placed in the divergent side of the nozzle and glued to the nozzle wall. Note that the glue should be dry before firing to avoid a misfire.

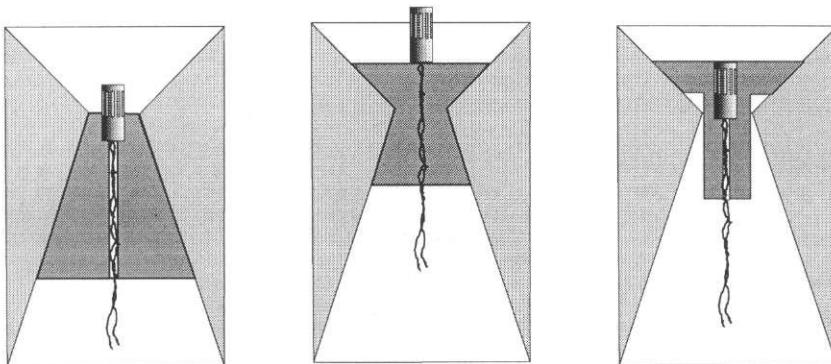


Figure 3.15. Different types of nozzle igniters.

This system was adopted by BVRO. A second method uses molten zinc-sulfur poured into the nozzle, covering both divergent and convergent parts of the nozzle. BVRO originally developed this method for potassium nitrate-sugar rockets, but NERO used it extensively for zinc-sulfur rockets. The drawing on the right shows a wooden plug placed in the convergent part of the nozzle, mainly used by NERO.

The ignition can be made easier by providing a layer of low dense propellant, in contact with the igniter.

Because NERO experienced several misfiring times in 1978 with the 3/1 composition, the *front-end ignition* was suggested by BVRO.

3.7.2. Front-end ignition

The igniter is placed at the front end of the rocket chamber. Since this type of procedure permits a maximum pressure in zinc-sulfur rockets. It is obviously more successful than nozzle-end ignition. One disadvantage, however, is that it is more difficult to manufacture. To prevent preliminary exhaust of unburned propellant, front-end ignition must be combined with a strong plug in the nozzle.

3.7.3. Central tube ignition.

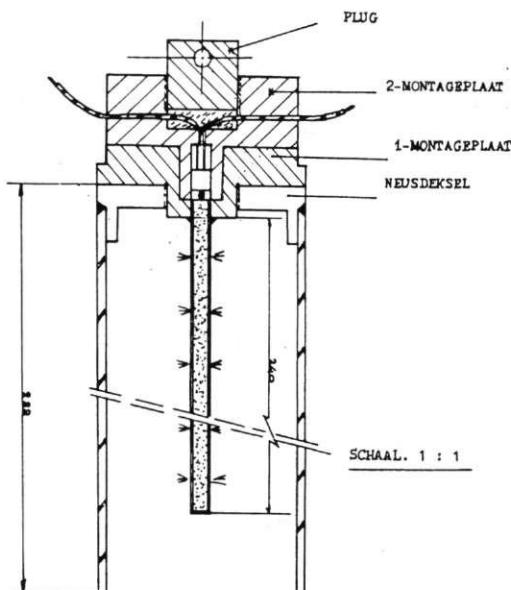


Figure 3.16. central tube ignition as applied by NERO

Since it is possible to ignite the propellant from the front end of the rocket, it must also be possible to ignite the grain from the middle. This technique, developed by G.Dörr (NERO), consists of a tube filled with powdered zinc-sulfur in which holes are drilled. See figure 3.16. Although very efficient it introduced the danger of using too much black powder and hence of a building up of too much gas, and thus pressure, at the ignition phase.

3.7.4. Influence of the igniter type on the thrust curve

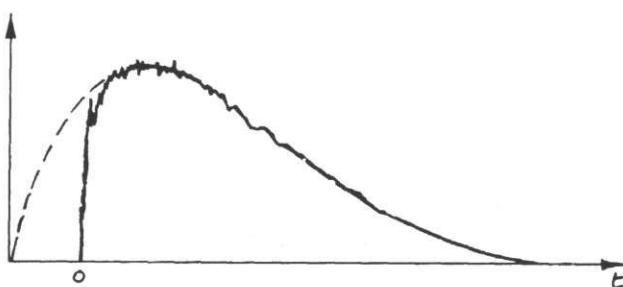


Figure 3.17. Effect of the burst pressure of the diaphragm on the progressive part of the thrust-time curve

NERO tests indicated that central tube ignition produces longer burning times (about 10% more) and a higher specific impulse (about 13%). It is possible that in the case of central tube ignition, more zinc-sulfur reacts before the diaphragm bursts resulting in less unreacted zinc-sulfur being expelled at the start.

With any type of igniter, the diaphragm burst pressure in the nozzle is very important. The higher the burst pressure, the higher the pre-thrust pressure in the rocket motor. Consequently, the higher the burst pressure, the more the chemical reaction is completed and the shorter the progressive part in the thrust-time curve. See figure 3.17.

3.7.5. The igniter

It is advisable to use only professional igniters. These igniters are safe and reliable. Electric current develops heat in a heat resistant wire, which in turn ignites a very small amount of easily ignitable product, like black powder, or a mixture of potassium perchlorate with carbon black and sulfur. In the SWALLOW motor (figure 2.1.), NERO used a mixture of black powder, BaN₃, Mg, and PbO₂. However, it is not certain that such complex compositions are necessary.

3.8. Preparing powdered zinc-sulfur propellants

Dusted zinc powder and flower sulfur are needed to prepare zinc-sulfur propellants. In general, technical grade will do.

Before use, zinc and sulfur should both be sufficiently dry. This can be a problem when the ingredients have been stored for a long time in humid spaces. Zinc and sulfur can be kept free of humidity by storing them in a flask with a bag of well-dried silicagel. Silicagel is a crystal that absorbs water reversibly. When saturated, the crystals are white. At elevated temperatures, the crystals loose their water and become blue. A drying oven can also be used. The oven should not heat the sulfur to its melting point (112°C). These precautions are not strictly necessary since neither zinc nor sulfur is hydroscopic, but depending upon the storage circumstances, they will absorb some water. Dried ingredients will also increase the reliability of the rocket performance, as it generates a more constant quality propellant.

The second step is grinding the sulfur. This is necessary since it normally contains lumps that would not easily mix with zinc. After sifting the sulfur, the exact amounts of zinc and sulfur should be weighted separately then mixed together. Mixing should be done carefully in a grounded (to eliminate static electricity) stainless steel reservoir with a wooden or plastic stick (not with a metal one) to avoid spontaneous ignition. Only small amounts should be used at a time, and the already mixed propellant should be stored far from the mixing place to prevent ignition in case of accident. After mixing no yellow spots should be visible. The propellant is now ready for use.

Depending upon the construction of the rocket, the propellant can as well be loaded from the nozzle side as from the aft side. Small amounts of powder should be added to the chamber, and than pressed gently with a stainless or a copper stick, slightly smaller than the inner rocket diameter. It is important not to use a stick that is too small, since the density over the length of the rocket chamber will differ too greatly. The loading can be performed in 10 or 20 times.

The reason for using copper or stainless steel sticks is to prevent sparks which may occur when contact is made with the inner wall. However, this may only occur in a metal-metal contact, so only in the case that no coating is applied to the inner wall.

When the rocket is filled from the top, a plug should be put in the nozzle to prevent propellant spillage. In this case it can be difficult to get the same density over the full length of the rocket, since the front disk is not yet mounted. It is therefore better to load the rocket from the nozzle side. This has the advantage of creating a low-density propellant layer near the igniter when nozzle ignition is used. Another advantage is that it does not put the igniter under pressure.

3.9. In flight behavior of powdered zinc-sulfur motors

Until 1989 it was believed that the powered zinc-sulfur rockets behave identically in flight as on the ground.

After a 1988 launching campaign at Mourmelon in France, Dirk Van Gelderen from NERO analyzed the pictures he had taken of the launch of BVRO (the Goddard) and NERO rockets (the E34) and concluded that the burning time was much shorter than was expected from the thrust-time diagram. Using the film he had taken, he measured the altitude of the rocket in function of time and sent me the information. This information was used to analyze the first phase of the rocket flight in terms of speed, and acceleration. And the result was indeed surprising. It was shown that the acceleration of the rocket, and hence its thrust, was much larger than what was expected. In fact, we reached *values of in-flight thrust which are several times (almost up to 4) larger than the ones measured on the test bench!* This means that ground measurement of the thrust curve is of limited value for flight purposes, unless we can correlate both.

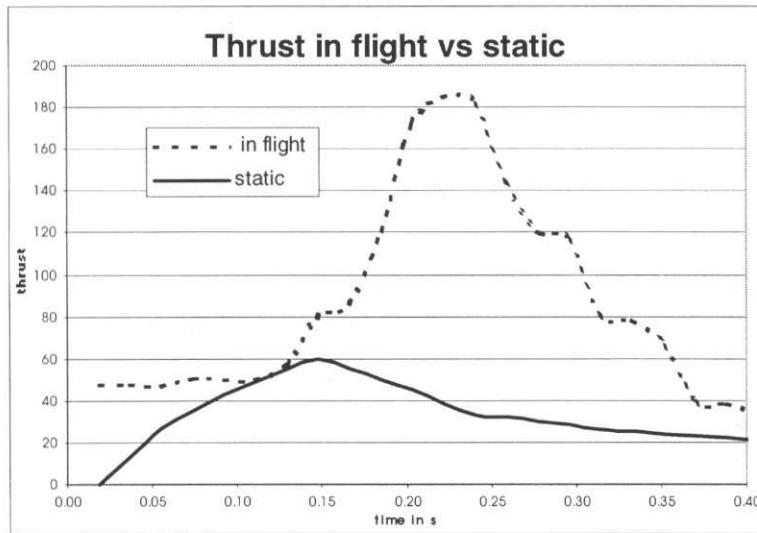


Figure 3.18. The first period of the in-flight thrust (blue) compared with the static thrust (red) - NERO E34 flight.

The in-flight thrust is clearly a function of acceleration, which in turn is a function of thrust. This is a self-increasing mechanism leading to strong accelerations and thrusts.

The explanation for this phenomenon must be sought in the increase of the solid particles' velocity in the nozzle due to the greater acceleration. The solid particles dominate the mass flow, as they represent more than 90% of the total mass. From the zinc-sulfur model (see chapter 3), we know that even small

changes in the slip factor, which is the ratio of the speed of the solids to the speed of the gas stream, causes significant changes in the mass flow.

There are also indications that in flight, chamber pressure is greater than during static testing. For this we have no explanation at this moment.

CHAPTER 4

HOT CAST ZINC-SULFUR PROPELLANTS

Hot cast zinc-sulfur is a very interesting alternative to the powdered propellant. This is made possible when the propellant is heated above 112°C, when sulfur becomes a low viscous liquid in which the zinc particles are suspended. After cooling, the propellant is very hard and strong, and of a very high density (3,2 gr/cm³ to 4,4 gr/cm³, depending upon the composition). In Europe, J.S.-SIVRY from Belgium was among the first to use hot cast zinc-sulfur intensively.

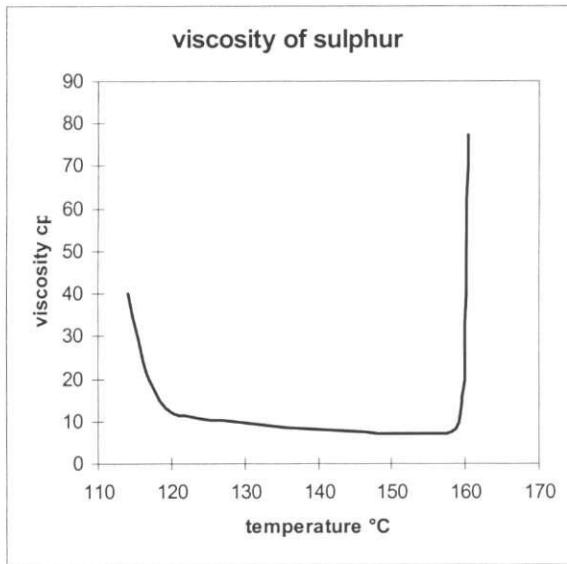


Fig.4.1. the viscosity of sulfur as a function of temperature

4.1. Experiments by J.S.-SIVRY

The preparation of the propellant is as follows. Technical grade zinc and sulfur are used in a ratio of 3/1 by weight. The powder is mixed for 1.5 hours using alternate rotation. After mixing, the propellant is melted in a pan in a thermostatic furnace at 145°C. When all the propellant is liquefied, it is poured into the rocket chamber; To remove the air, the mixture is vibrated during the first part of the cooling, till there is no more liquid. The rocket chamber is then rapidly cooled in a cold water bath. At later stages the melting was executed under a CO₂ atmosphere*.

* it is strongly advised NOT to use CO₂ as an "inert gas" as it can react with both zinc and sulphur to create ZnO and SO₂. N₂ should be preferred instead.

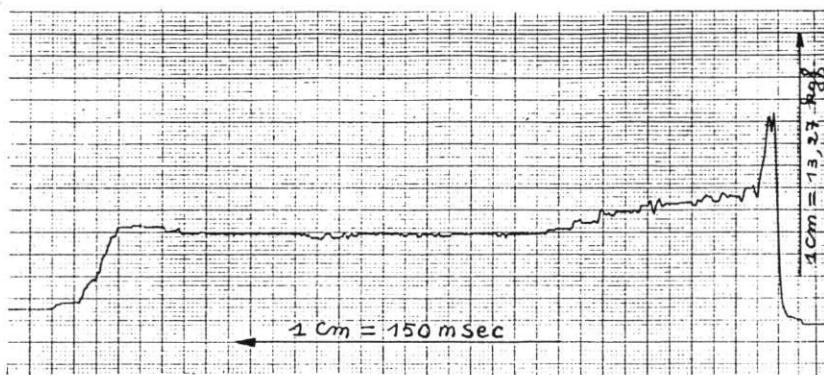


Fig.4.2. Thrust curve of a coated hot cast Zn/S 3/1 grain (J.S.SIVRY)

J.S-SIVRY made several types of cast zinc-sulfur grains. The most common types had direct contact between propellant and wall. In later rockets the propellant grain was coated with a silicon layer (thrust curves of these type of rockets are shown in figures 4.2 and 4.3).

The coated propellants have a flatter thrust-time curve and in one case (fig.4.2.) almost a totally constant thrust.

A propellant density of 4 gr/cm³ is normally achieved with the 3/1 mixture. This is about 1.5 times more than the powder !

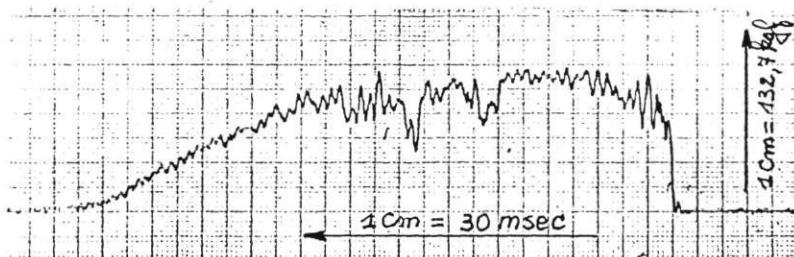


Fig.4.3. Thrust curve of an uncoated hot cast Zn/S 3/1 grain (J.S. SIVRY)

4.2. Experiments by BVRO in the 1970s.

Also the BVRO experimented with hot cast zinc-sulfur propellants. In a first period, a propellant ratio of 2/1 was used with and without the addition of aluminum.

In the first test, (ref.19), the propellant was liquefied in the rocket chamber by an electric heating wire spiraled around the outer rocket wall. The grain was of the bar type (no central hole) with a ratio of burning area over throat area of 9 (GX-3). The propellant density was 3.8 gr/cm³ (note that this has to be lower than in the J.S. SIVRY case because there is less "heavy" zinc than in the case of 3/1). After ignition, the propellant burned for several seconds without delivering any measurable thrust.

In a second type of rocket (ref.20), some aluminum was added to the 2/1 propellant (0.5% to 2%). After mixing, the propellant was heated in an electric pan till total liquefaction*. The propellant was then poured into the cold rocket chamber, which was provided with a steel rod to create a cylindrical hole after becoming solid. With the propellant still hot, water was poured in the center of the rod. This reduced the rod's diameter, which made removal from the tube easier.

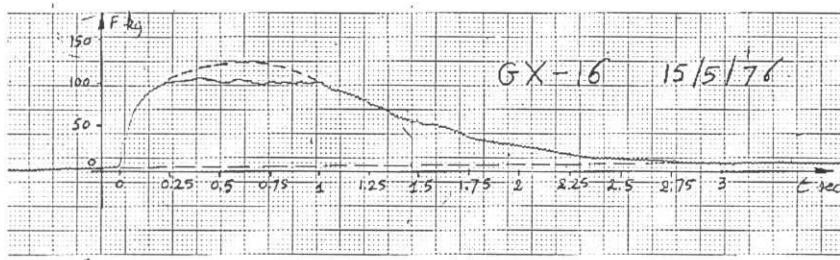


Fig.4.4 . Thrust-time curve of a hot cast Zn/S 2/1 +1% Al propellant rocket (GX-16)

The specific impulse measured in this type of rockets range from 45s to 49s with an aluminum content going from 1% to 2%. The propellant density did suffer somewhat from the higher aluminum content due to a higher viscosity of the liquid.

In a third series of tests, the propellant was cross shaped, and no aluminum was used (ref.20). Although the ratio of burning area to throat area was very high (2300), the rocket's burning rate was very low and no measurable thrust could be obtained. In these tests the mean propellant density was 3,76 gr/cm³.

4.3. A granulometric study

J.S.-SIVRY made a granulometric study of the hot cast 3/1 zinc-sulfur propellant (ref.18). This study has shown that the zinc particles enlarge in the liquid phase. Starting at 6 µm the mean zinc particle diameter becomes 40µm after 540 seconds!

* heating on an electric plate is not safe as temperature cannot sufficiently be controlled and hot spots may occur

The particles enlarge rapidly between 80 and 240 seconds after the liquefaction starts. Enlargement is nearly completed after 540 seconds.

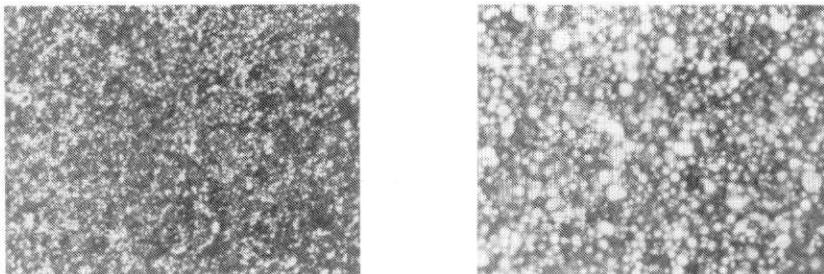


Fig.4.5. Particle size evolution (J.S.Sivry)

The degree to which particle size influences burning rate or rocket performance is not known. However, at J.S. SIVRY they concluded that the propellant should be cooled quickly.

4.4. Zinc particle distribution

Since solid zinc particles are heavier than the liquid sulfur, sedimentation can be expected in these propellants.

Van Schaik from NERO measured the density of cuts made from a Zn-S-Mg grain. Measuring the densities at various distances from the top of the grain revealed however no sedimentation.

J.S.-SIVRY also studied the segregation phenomenon. Cuts were made of grains cooled at various speeds. It was shown that in slowly cooled grains sulfur migrates to the center in the top section of the grain. This can be very severe as shown in ref.18. No segregation was found when the cooling was very fast, indicating the importance of the cooling rate. The following pictures show cuts from slow (L) cooling grains. The sulfur concentrates at the top can be clearly seen. This is not the case in fast cooling. The pictures also show a hole at the top end of the grain caused by propellant shrinkage. The many craters indicate the presence of air bubbles in the grain.

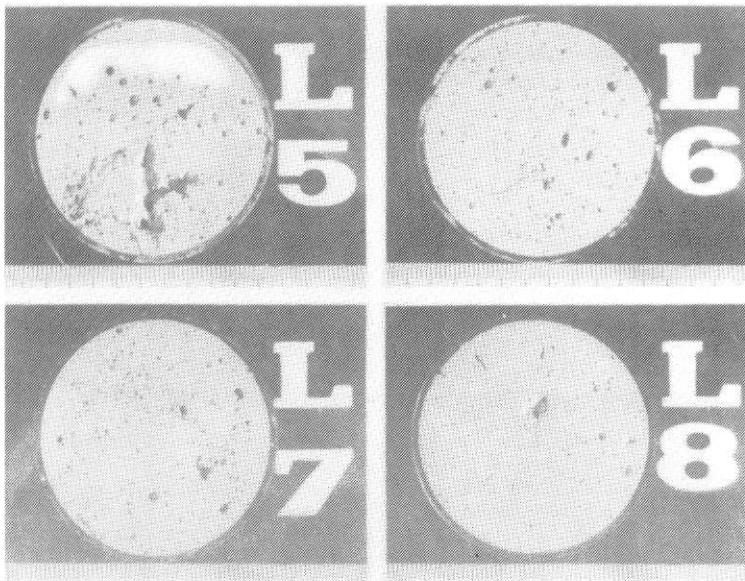


Fig.4.6. Cuts from hot cast zinc-sulfur grains - slow cooling (J.S. SIVRY)

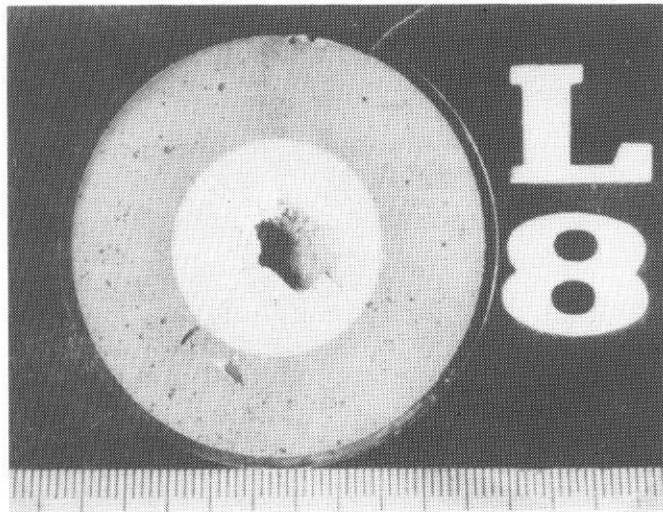


Fig.4.7. Top cut of hot cast zinc-sulfur grain - slow cooling (J.S.SIVRY)

4.5. Recent tests by VRO

The objective of these tests, starting in 1998, was to develop a safe, reliable and powerful propellant based on hot cast zinc-sulfur. Up to 10% of aluminum was added to improve the specific impulse. Two configurations were made: one with an inner diameter of 2.54 cm (called ZAS2.5) and one with 5.4 cm (called ZAS5). Except for the smaller rockets, where the grain consists of one single block, up to three blocks were used in the larger motors. Propellant densities ranged from 3.4 g/cm^3 to even 3.89 g/cm^3 (the theoretical density of these mixtures is 4.13 g/cm^3).

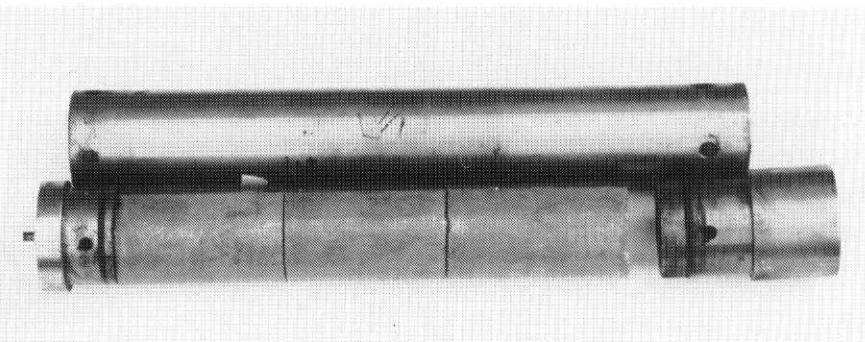


Figure 4.8. ZAS5-3 with his 3 (still uncoated) propellant blocks

losses and to stabilize the temperature. In later trials, after liquefaction, the recipient was put on an iron block and insulated all around (except the bottom) to have all the heat dissipate through the bottom. This procedure prevents the

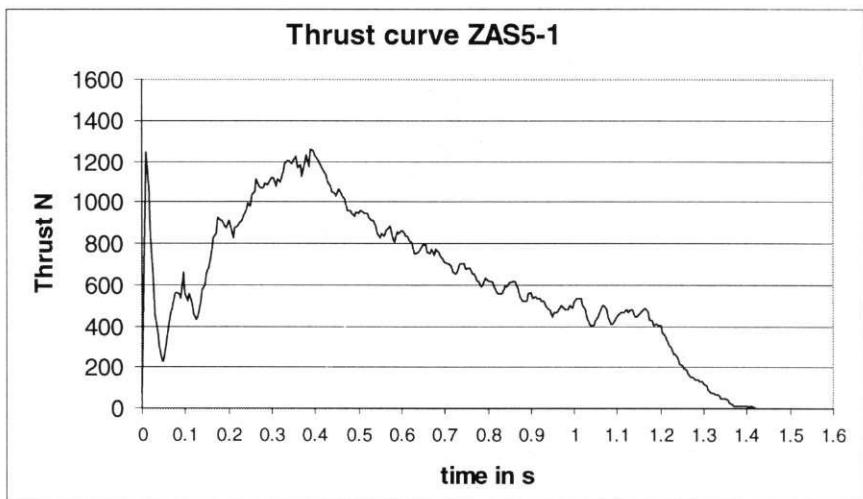


Figure 4.9. Thrust diagram of ZAS5-1

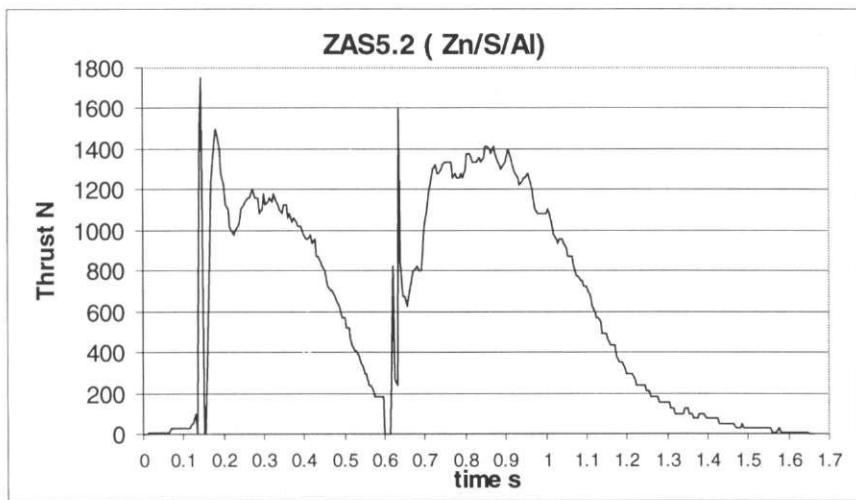


Figure 4.10. Thrust diagram of ZAS5.2

formation of holes and resulting in higher propellant densities (mean value 3.71 g/cm³). The top of each grain was cut off. All blocks were coated afterwards along the cylindrical part. When the thrust diagrams of the different tests are put together, we get picture 4.12. This picture also gives the smaller ZAS2.5-1, once the real thrust curve and once the curve scaled up to the nozzle diameter of the ZAS5 rockets. The curves of ZAS5-2 are presented as separate curves.

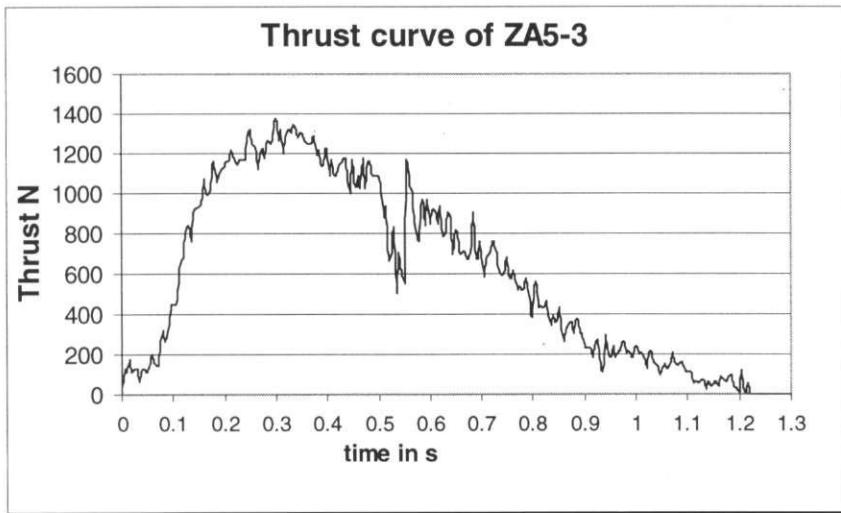


Figure 4.10. Thrust diagram of ZAS5.2

It is easy to see that most of the curves have an analogue trajectory (this is also the case for the smaller ZAS2.5). Some curves are somewhat steeper at the beginning, but all reach a maximum at more or less the same value (1200 N-1400 N) of the thrust. After the maximum, we get a decrease in the thrust level

In these tests we measured specific impulses ranging from 50s to 56s with 10° outlet nozzles.

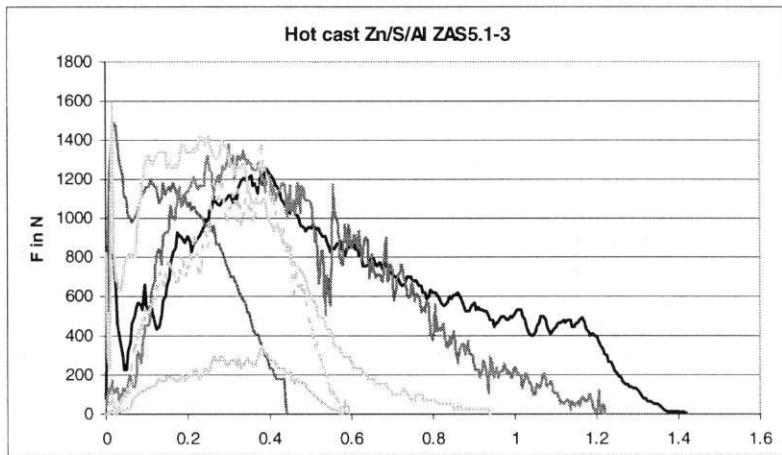


Figure 4.12. thrust curves from ZAS5-1, ZAS5-2, ZAS5-3 and ZAS2.5-1

4.6. The burning rate mechanism.

From the different experiments with hot cast zinc-sulfur rockets, it is now certain that the propellant burns in parallel layers. That the thrust diagrams not always show what is to be expected from this type of burning has specific reasons, which will now be explained.

For some time we have considered the considerable shrinkage of the liquid propellant during cooling to be responsible for at least part of the explanation. Indeed, at 20° the density of sulfur is 5 to 10% lower than at 120°C.

The heat released through the wall during the cooling process, whereby the outer parts of the grain cool quicker than the inner parts, may cause cracks and holes in the center of the grain. It was assumed that through the holes and cracks, essentially along the center of the grain, the grain burns partly from the inside to the outside. It was also assumed that when no liner (inhibitor) is applied to the outer surface of the grain, which is mostly the case when the hot liquid is poured directly into the rocket chamber, a space will be created between the chamber wall and the grain after cooling. As a consequence, we expected the grain to burn essentially from the outside to the inside. This problem was corrected rather easily when the grain is

prepared in a separate mold with a diameter smaller than the rocket chamber, and when an inhibitor is applied. In some cases it may be possible to apply the liner first to the inside of the rocket chamber and then pour in the liquid propellant. In this case the inhibitor must be sufficiently thick and elastic to compensate for dilatation. Also the grain must stick to the liner.

Although very attractive to explain how hot cast zinc-sulfur grains burn, the theory of the central hole and the creation of cracks raises a number of objections as the ZAS experiments showed:

- The first point is that to cause the fast thrust increase, as seen in the ZAS rockets, the first blocks would always have to have been oriented with the "hole" side towards the nozzle. Except for the ZAS5.3 this was never registered, but for this to be the case in 4 out of 4 tests would have to be a coincidence.
- A second point is that we should see a strong peak in the thrust curve at the ignition of each following block oriented that way. We never did.
- ZAS2.5-1, with half the grain diameter of ZAS5, should reach its peak in about half the time. However, it reaches the top after about 0.4s.
- Since the top of the thrust curve has each time more or less the same value, it would mean that all cracks are of the same length.
- Inspection of the rockets after the tests revealed that the inhibitor at the aft end was always intact, indicating cigarette burning.
- When we compare the total burning time to the total grain length we find an almost linear correlation. This again indicates cigarette burning.

In the tests with the ZAS-rockets, we observed the following phenomena:

- there is a significant ignition delay for the main propellant block when ignited with powdered zinc-sulfur. This delay goes up to several tenths of seconds.
- after ignition, the thrust rises rapidly, reaching a maximum after 0.2 - 0.4 s (which is more or less constant), and decreases mostly slowly to a lower thrust level or even to extinction;
- when two different propellant blocks do not make sufficient contact, thrust may fall (even to zero), before a new block works properly;

To understand what can happen we have to consider the following. Sulfur is a non-metallic element with a low heat conduction coefficient, which starts boiling at 444°C. The gases are very reactive and attack metals. Zinc is a very heavy metal (7.4 g/cm³) with a high heat conduction coefficient (0.1 cal/gKs), which boils at 691°C. Aluminum is a light metal (2.7 g/cm³) with a very high heat conduction coefficient (0.3cal/gKs), which boils only at 2600°C.

The physical characteristics of zinc-sulfur-aluminum hot cast propellants differ in the following way from classic composite propellant:

- ⇒ The products that constitute the propellant are single elements, which means that they will boil at a specific temperature and do not decompose as plastics or salts (typical solid oxidants) do.
- ⇒ The boiling temperatures are very different.

- ⇒ At high pressures, the products do not behave as ideal gases (Zn, ZnS) but will instead be in equilibrium with its solid or liquid state.
- ⇒ Except for sulfur, they conduct heat much faster.
- ⇒ The temperature at which both oxidant (sulfur) and fuel (zinc and aluminum) gases are formed is much higher.

The very high heat conductivity and the high boiling point of zinc are responsible for the difficulties in igniting this propellant. The temperature at the surface must be at least 709°C for a proper functioning, while heat is easily transferred away from this surface towards the inner side. The preheated zone in this type of propellant is much larger than in composite propellants. In cases where the heat flow from outside towards the propellant is not high enough, but of a long duration (which is the case at ignition and between insufficiently contiguous propellant blocks), the propellant block may heat up significantly (up to several centimeters inside the grain).

The difference in boiling points is responsible for different states of burning, as will be explained now.

1. **In the first burning mode (ignition by powdered zinc-sulfur), the heat transfer towards the propellant surface is insufficient to raise the temperature above 709°C.** As a consequence **only sulfur will evaporate.** Zinc and aluminum remain solid or liquid. However, this sulfur will attack the zinc and aluminum particles at the surface, creating sufficient heat to continue the process. Part of the heat will leave with the reactants, another part will be transferred to the propellant. The stability of this burning depends upon the rate at which the propellant is heating up (heat conductivity and hence propellant composition) and the possibility for building up pressure (ratio of burning surface to throat surface). The reactants of the process are ZnS essentially as a gas (and thus at low temperature), and zinc (because we have an overdose of zinc in the propellant). This burning has often been observed during misfire: the propellant burns but at a very slow rate and delivers no thrust.
2. **In the case where the temperature at the grain surface has risen above the boiling point of zinc (709°C),** due to a sufficient heat transfer towards the grain, the reaction between sulfur and zinc will take place mainly in the gas phase. This reaction is very fast and delivers enough heat to the surface to continue the evaporation. When aluminum is added, it will only evaporate when the temperature is above 2600°C, which is presumably not the case at the surface. So we suppose that zinc and sulfur gas transport heat while sulfur attacks the solid aluminum. Chamber pressure is now building up.
3. **When the reaction pressure becomes high, zinc will no longer be only gaseous, but will come in equilibrium with its liquid state.** As a consequence, it will be increasingly difficult for zinc to evaporate. The reaction rate depending upon the partial pressure of zinc will be much lower than in the second case.

We now believe that the explanation for the different phase in the thrust curves is the following:

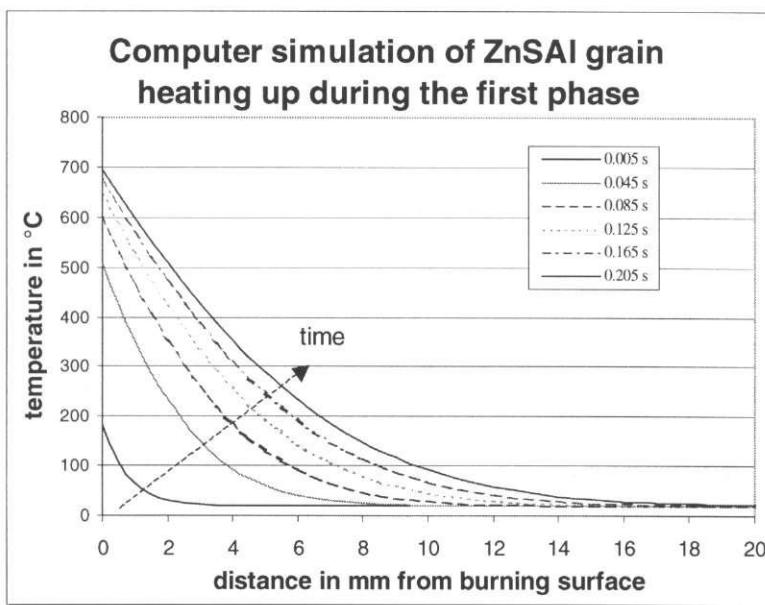


Figure 4.13. Temperature increase of the grain during the first (heating up) phase

1. **Preheating phase:** during the whole period that the hot reactants (ZnS and Zn) from the ignition powder are still in the rocket motor, heat is transferred towards the solid propellant block. Due to the very high conductivity of the solid grain (67% Zn, 10% Al), the block is heating up, draining away heat from the grain surface, causing a slow temperature rise (it takes about 0.2 to 0.4 s to raise the surface temperature to 709°C, the boiling point of zinc) at the surface. As a consequence, sulfur will first boil (444°C) and react with the solid zinc and aluminum. As this is a *surface reaction* it is very slow. More and more heat is pumped into the grain, which is heated over a long distance. It is estimated that the thickness of the heated area of the grain which is in the order of 10 to 20 mm. (see figure 4.13).
2. **Transition phase:** after some time (0.2 to 0.4 s) the temperature at the surface has risen to the boiling point of zinc. This time zinc gases thus created will react with the sulfur gases. This *gas reaction* is very fast. Very high temperatures are now created near the surface, heating it and gasifying sulfur and zinc. Pressure builds up. Since the propellant block at this moment is at its hottest, the reaction will be extremely fast (during only milliseconds the burning rate may be up to more than 100 cm/s). The thrust curve goes up.
3. **Maximum thrust :** since the burning area reaches now progressive regions of lower temperature in the block, the temperature distribution in the grain becomes less pronounced (see figure 4.14), the reaction rate will decrease (see figure 4.15). As a consequence the thrust curve will reach a maximum. The reaction rate now equals the exhaust rate.

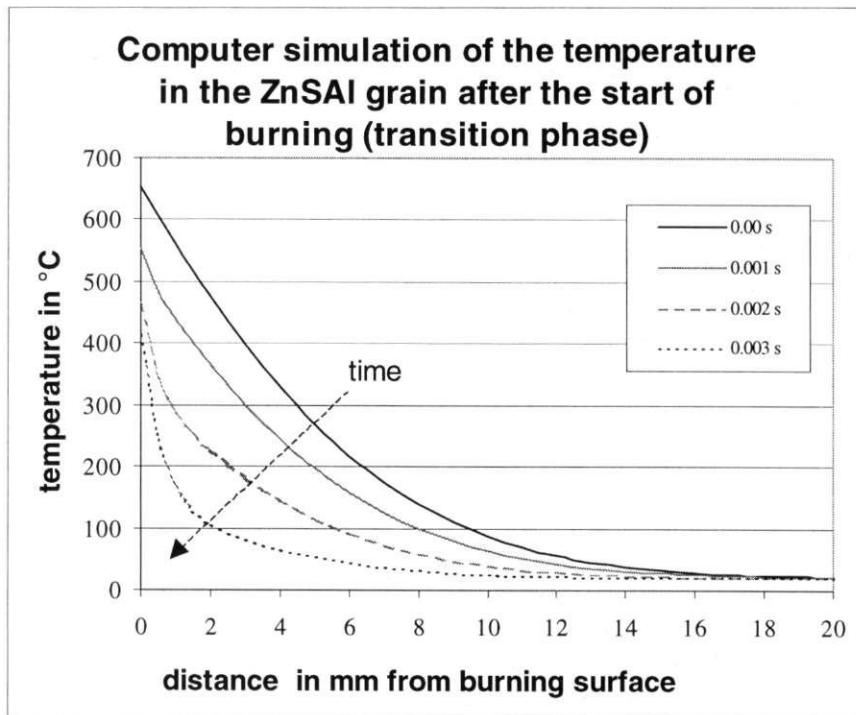


Figure 4.14. Temperature distribution during the transition phase

4. The burning area continues reaching sections of lower temperature, decreasing further the burning rate and hence the thrust.
5. An equilibrium may be reached (see figure 4.9 of the ZAS5.1 curve) when the heat conductivity of the grain is not too large, permitting stable burning. Whether this will happen depends upon the sulfur content. It is experimentally demonstrated that above 25% sulfur content, the conductivity is low enough to continue the reaction. With lower sulfur contents, the reaction may finally stop as can be seen in figure 4.11. with ZAS5.3.
6. When one propellant block is consumed the next block should start burning. Whether this will happen immediately or with some delay, depends upon the **fairness of the contact between both blocks**. When the contact is loose, the second block will not ignite immediately and pressure will drop. We will have the situation described under point 1 and the whole story repeats itself (see figure 4.10. ZAS5.2). When there is a fair contact, burning will continue, since heat is normally transported to the next block.

This theory also shows that burning cannot occur in fine cracks, since heat is immediately taken away by the very high conductivity of the material.

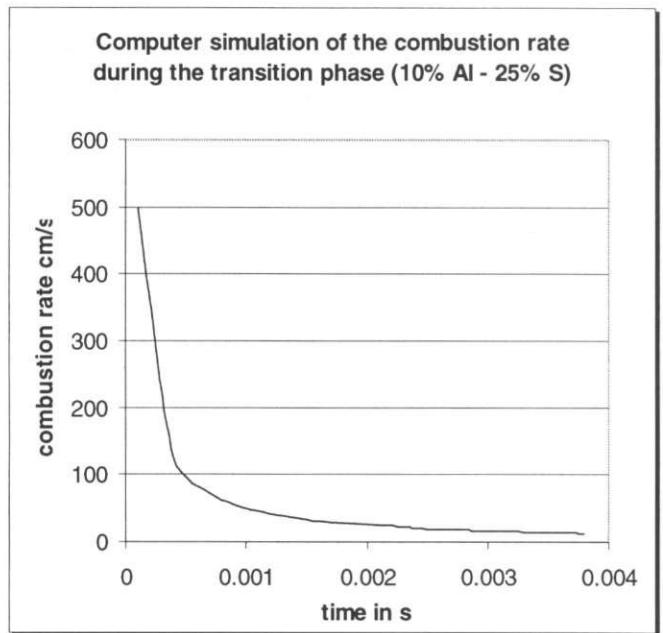


Figure 4.15. The burning rate during the start of the transition phase as a function of time



Figure 4.16. Thrust curve of ZAS5-4

The great thing about hot cast zinc and sulfur rockets is that, at least at moderate pressures, the grains burn in parallel layers and at a very high rate. This means that it is possible to use the cigarette or other types of grain configurations, according to

the desired rocket thrust. Burning times up to several seconds are possible with almost flat thrusts diagrams. In addition, densities are much greater than for the powder. We believe that with a proper melting procedure, this type of zinc-sulfur propellants may have a great future for amateur rockets.

That the coated J.S.SIVRY rockets behave somewhat different is probably due to the higher sulfur content and hence lower conductivity. Less heat is conducted through the grain and the propellant burns at a nearly constant rate (see figure 4.2.). This was also shown in the ZAS5.4 test (see figure 4.16), where the sulfur content is 25%, and a grain with a central hole was used. The grain burns nearly theoretical at a rate of 5 cm/s.

In figure 4.3. the thrust curve from one non-coated grain is shown. Here the burning time is somewhat less due to the heat flow along the chamber wall, progressively heating up the outside of the grain. As a consequence we get a faster burning at the sides than in the middle. The thrust is higher and the duration somewhat shorter.

The great thing about hot cast zinc and sulfur rockets is that, at least at moderate pressures, the grains burn in parallel layers and at a very high rate. This means that it is possible to use the cigarette or other types of grain configurations, according to the desired rocket thrust. Burning times up to several seconds are possible with almost flat thrusts diagrams. In addition, densities are much greater than for the powder. We believe that with a proper melting procedure, this type of zinc-sulfur propellants may have a great future for amateur rockets.

4.8. The influence of the sulfur content on the burning rate

From the different experiments conducted with hot cast zinc-sulfur, we believe that we have enough evidence to conclude that the sulfur content in the propellant plays a determining role in the burning rate. This is shown in figure 4.17 where for some experiments the burning rate is plotted against sulfur content.

At sulfur contents below 25%, the burning rate becomes undetermined and can be extremely high or very low as already explained in section 4.7. It all depends upon the past temperature history of the propellant in the motor. A 25% sulfur content grain without high conductive ingredients like aluminum, is quite stable and burns at about 10 cm/s. Adding up to 10% of aluminum to this mixture will make the propellant more heat conductive and hence history dependent. This propellant however still seems to have an equilibrium burning rate of about 10 cm/s (see the difference in thrust diagram between figure 4.2 - no aluminum - and 4.9 - 10% aluminum). At 28% sulfur, even with high amounts of aluminum, the burning rate was very stable. This was also the case with 33% sulfur and an aluminum content varying between 0.5 and 2%.

In how far the aluminum content influences the burning rate is not known, although from the comparison between the Sivry motor and ZAS5.1, we believe that at sufficient high sulfur contents this influence is very small.

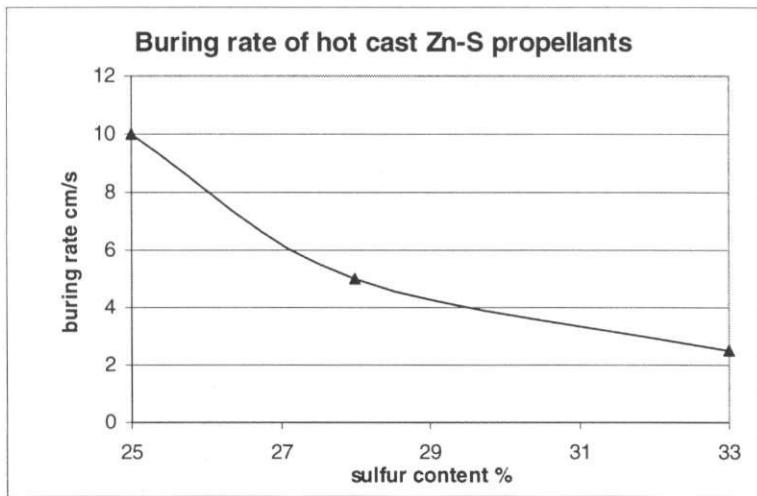


Figure 4.17. Relation between the sulfur content in the hot cast propellant and the burning rate

The reason why the burning rate is so dependent on the sulfur rate, must probably be sought in the fact that at high sulfur contents the metallic particles do not longer create high heat conductivity bridges throughout the propellant, allowing fast heat transfer, but are interrupted by sulfur particles hereby decreasing the conductivity. *At higher sulfur contents, the grain is more easy to ignite and will burn more stable.*

4.9. Some safety aspects

As already explained, hot cast zinc-sulfur propellants can generally be made safely. The major safety problem stems from the particular viscosity curve (figure 4.1). When heating beyond 158°C, the viscosity will rise again, which may lead to an erroneous interpretation of the temperature of the liquid, leading to a decision to increase the temperature, even to the point of spontaneous ignition.

Melting can be done safely in a large oil bath, where the temperature is kept below 170°C.

CHAPTER 5

OTHER MODIFICATIONS

There is little information available about other modifications of zinc-sulfur. One method consists in *pressing the powder* to very high densities. N. Fiser and B. Zecevic, from the Rocket Research Society at Sarajevo, reported in 1980 on this modification. For Zn/S 2/1 mixtures they got densities of up to 3.08 gr/cm³ (applied pressure 900 bar). They reported difficulties in ignition as could be expected from very dense propellants, since a critical gas penetration is more difficult to attain. Chamber measurements revealed pressures around 60 bar.

Although an alternative for hot cast zinc-sulfur, it is probably much more difficult for amateurs to use, since it requires high pressure equipment.

More interesting seems to be cold-casting the mixture by using solvents such as alcohol or even water. When small amounts of a solvent are added to the powder the propellant will turn into mud, which can be cast into a rocket motor. It takes a few days before all the solvent is removed, after which the propellant is relatively hard and dry. The use of solvents, however, is not without danger as it releases low boiling gases in the rocket chamber, of which but little is needed to create very high pressures during burning and hence increase the risk of explosion.

PART 3

CALCULATING ZINC-SULFUR ROCKETS

CHAPTER 6

NOZZLE CALCULATIONS

When important amounts of solid or liquid particles occur in the reaction products at combustion, the nozzle equations established for ideal gases are no longer valid. Indeed, these particles will not exchange heat perfectly with the environment and as a result there will always be a difference in temperature, called the *temperature lag* (because of the expansion of the gas, the temperature of the particles will always be higher than that of the surrounding gas). On the other hand these particles cannot gain speed through expansion, but need drag from the gas stream to accelerate. This creates a *speed lag*.

Calculations show that heat and impulse transfer between solid particles and gas, is only fairly complete, when the solid particle diameter is smaller than 10^{-4} cm. According to Stonecypher (ref.2) the region of interest in particle size is from 1 to 10 microns in diameter. Above 10 microns and below 1 micron, additional effects are small. He has also shown that in addition to particle size, the ratio of nozzle throat diameter to outlet diameter has to be taken into consideration.

The main goal of this chapter is to derive general expressions applicable to streams with large particle content.

6.1. Thrust

When the velocity of the fluid is **homogeneous** in any section of the nozzle, the thrust can be written as:

$$F = m.u_e \quad (6.1)$$

When two phases occur with different velocity and under the assumption that in both phases the velocity is constant, the thrust becomes:

$$F = \dot{m}(1 - x_e)u_{ge} + \dot{m}x_e u_{se} \quad (6.2)$$

6.2. Gas velocity at the end of the nozzle

The velocity of the solid particles at any section, can be expressed as a fraction of the gas velocity, or:

$$\frac{u_s}{u_g} = \alpha \quad (6.3)$$

Putting relation (6.3) into (6.2), and comparing with (6.1), we get for the conditions **at the end of the nozzle**:

$$u_{ge} = \frac{u_e}{1 - x_e + \alpha_e x_e} \quad (6.4)$$

So, when we know the velocity delivered by the nozzle (based on thrust measurements), we can compute the gas velocity u_{ge} provided that x_e and α_e are known. As can be seen from formula 6.4, u_{ge} is always larger than u_e since x_e and α_e are by definition situated between 0 and 1.

6.3. The exhaust velocity u_e

The enthalpy drop over the nozzle, is transformed into kinetic energy of the gas and solid particles

$$\frac{1-x}{2}u_g^2 + \frac{x}{2}u_s^2 = \Delta H \quad (6.5)$$

Because of relation (6.4), we get at any point in the nozzle:

$$u = \frac{1-x + \alpha x}{\sqrt{1-x + \alpha^2 x}} \sqrt{2\Delta H} \quad (6.6)$$

$$u_g = \sqrt{\frac{2\Delta H}{1-x + \alpha^2 x}} \quad (6.7)$$

This is a general expression, when u_s and u_g are uniform for all gas and all particles. From this expression, we see that the enthalpy drop is not completely transformed into exhaust velocity. This is, of course, due to the velocity lag and the fact that particles have a higher temperature than the gas phase.

The most important thing to find now is the enthalpy drop.

6.4. The enthalpy drop ΔH

As already explained, the enthalpy drop can only be found, when we know the temperature lag between the solid and the gas, and this depends upon the particle size distribution. The general expression for ΔH at any cross section of the nozzle is:

$$\Delta H = H_c - \int_{298}^{T_g} Cp_s dT - (1-x)\Delta H_s^{T_g} - x \int_{T_g}^{T_s} Cp_s dT \quad (6.8)$$

The explanation is the following:

- we first heat all reaction products under solid form to the temperature of the gas T_g which will be lower than the solid phase because the gas loses its temperature by expansion (which is instantaneous), while the particles loose their temperature by radiation, convection and evaporation.
- at T_g we vaporise the $(1-x)$ fraction (which is the gas fraction).
- the remainder "x" is further heated to its temperature $T_s > T_g$.

H_c is the heat content in the reaction chamber, which at the start is equal to the heat of reaction. Its value for isentropic expansion is calculated in chapter 7.

6.5. Mass flow calculations

The total mass flow can be divided into the gas flow and the particle flow:

$$\dot{m} = A_g \rho_g u_g + A_s \rho_s u_s \quad (6.9)$$

With the help of relation (6.3) we come to:

$$\dot{m}_s = A_s \rho_s u_s \quad (6.10a)$$

$$\dot{m}(1-x) = A_g \rho_g u_g \quad (6.10b)$$

And since $A_s + A_g = A$ (total area of the nozzle cross section), we find:

$$Ag = \frac{A(1-x)\alpha\rho_s}{x\rho_g + (1-x)\alpha\rho_s} \quad (6.11)$$

The total mass flow can now be expressed as:

$$\dot{m} = A \left[\frac{\alpha\rho_s\rho_g}{x\rho_g + (1-x)\rho_s\alpha} \right] u_g \quad (6.12)$$

This expression holds for any cross section of the nozzle.

CHAPTER 7

THERMODYNAMIC CALCULATIONS

So far the zinc-sulfur propellant has only been considered in a qualitatively way. However, we want to know why we come to these results and what will happen when composition and ingredients are changed.

A good thermodynamic model must be able to answer all these questions. Therefore it is very important to give zinc-sulfur propellants a thermodynamic basis. With this model, it will be possible to simulate certain circumstances on a computer, which would otherwise have to be tested in time-consuming experiments.

A thermodynamic system depends entirely on its data. This means that when there is not enough information available, assumptions must be made. However, because of the complexity of the problem, this will be inevitable.

7.1. The sublimation heat of ZnS

The sublimation heat as a function of temperature is not available in the literature. Therefore we have to develop an adequate relationship.

The reaction heat between solid zinc and solid sulfur at 298°K, to create solid ZnS at the same temperature is known to be between 45000 and 48500 cal/mole. When ZnS is above this temperature, the reaction heat has to be decreased by the heat content of solid ZnS at this temperature.



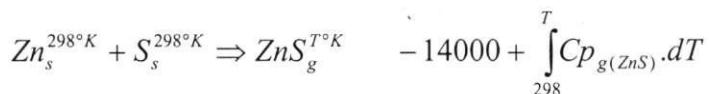
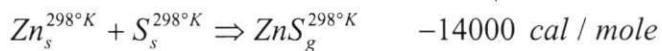
$$Zn_s^{298\text{°}K} + S_s^{298\text{°}K} \Rightarrow ZnS_s^{T\text{°}K} \quad \Delta H_v^{298\text{°}K} = -48500 + \int_{298}^T Cp_{s(ZnS)} \cdot dT$$

$Cp_{s(ZnS)}$ is the molar specific heat of ZnS. According to the literature its value between 273°K and 1173°K is

$$Cp_{s(ZnS)} = 12.81 + 0.00095 T - 194600 T^2 \quad \text{cal/mole K} \quad (7.1)$$

When the reaction between solid zinc and solid sulfur at 298°K yields gaseous ZnS, the reaction heat is - 14 000 cal/mole.

To calculate the heat of reaction for gaseous ZnS at T°K, we have to subtract the heat we need to elevate the temperature of ZnS_g from 298°K to T°K.



$Cp_{g(ZnS)}$ is the molar specific heat of gaseous zinc sulfide. Its value is given in the diagram figure 8.1. For the temperature range we deal with, an average value of 8.92 cal/mole is taken.

It is clear that the difference between the reaction heat to make solid ZnS at T°K and the reaction heat to make gaseous ZnS at T°K, is nothing else but the sublimation heat we are looking for:

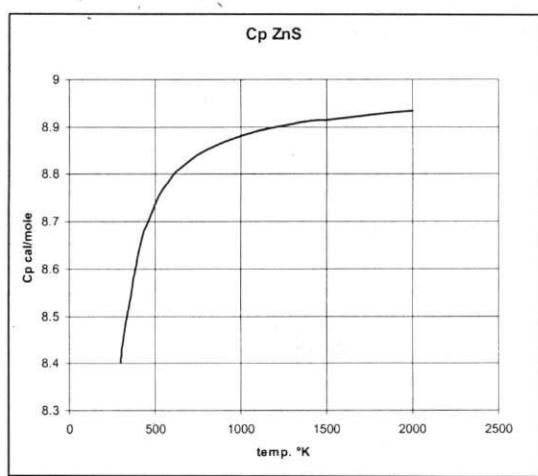


Figure 7.1. The specific heat of ZnS gas

$$\Delta H_{s(ZnS)}^T = -14000 + \int_{298}^T Cp_{g(ZnS)}.dT + 48500 - \int_{298}^T Cp_{s(ZnS)}dT$$

With:

$$\int_{298}^T Cp_{s(ZnS)}dT = 12.81T + .000475T^2 + \frac{194600}{T} - 4513$$

(valid up to 1173°K)

$$\int_{298}^T Cp_{g(ZnS)}dT = 8.92T - 2658 \quad (7.2)$$

The expression for $Cp_{s(ZnS)}$ is only valid to 1173°K. Since we have no data for higher temperatures, we will assume that the expression holds for the whole temperature range.

Under severe pressure and temperature, solid ZnS is transformed to the liquid state. This consumes energy. So instead of discussing only the transformation from the solid to the gaseous state, we should discuss a solid-liquid-gas transformation. However, we do not have enough data to do this. So we will leave it as it is. The margin of error is probably not very large.

$$\Delta H_{s(ZnS)}^T = 36354 + 8.92T - 12.81T - 0.000475T^2 - 194600T^{-1} + \Delta H_{f(ZnS)} \quad (7.3)$$

With $\Delta H_{f(ZnS)}^T$ the unknown fusion energy of ZnS.

7.2. The partial pressure of ZnS

For ideal gases, knowing the sublimation heat is sufficient to calculate the partial pressure of the gas in equilibrium with the solid phase. This relation can be found with Clapeyron's laws

$$\frac{dP}{dT} = \frac{\Delta H_s^T}{\Delta V \cdot T} \quad (7.4)$$

To make it useful, it is necessary to know the relation between the volume and the pressure. For an ideal gas where the volume of the solids to gas is negligible, we can use Boyle's law and write: $P V = R T$

$$\frac{dP}{P} = \frac{\Delta H_s^T dT}{R \cdot T^2}$$

In reality, however, there will be a strong deviation from the ideal behavior at high pressures, so that we need to write: $PV = z \frac{RT}{V}$

Hence we reach:

$$\frac{dP}{P} = \frac{\Delta H_s^T dT}{zR \cdot T^2}$$

Since we already know the sublimation heat as a function of temperature, and since we also know that the equilibrium pressure at 1458°K is 1 bar, we can find the pressure at any temperature by integration:

$$P_{ZnS} = \exp\left(\frac{1}{z}\left[-1.965 \ln \frac{T}{1458} - 0.00024T - \frac{18360.8}{T} + \frac{97300}{T^2} + 12.92\right]\right) \quad (7.5)$$

P_{ZnS} is expressed in bar. The relation is represented in figure 7.2 for different values of z .

The compressibility factor z is, in general, a function of pressure and temperature and is positive for high temperature values. In our calculations, we have adopted the formula:

$$z = 1 + \alpha / 100 * P_{ZnS} \quad (7.6)$$

with the following values for α : 0 (ideal gas situation); 0.05 ; 0.10 ; 0.15

As can be seen in figure 7.2, even small values of the compressibility factor will have a large effect on the pressure.

The same system used to calculate the vapor pressure of ZnS will also be used for calculating the vapor pressure of Zn. As will be shown in one of the next pages,

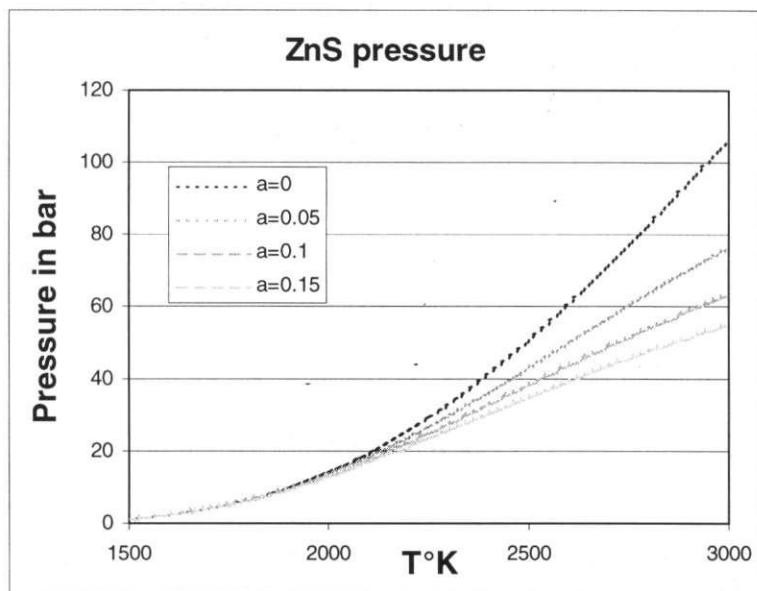


Figure 7.2. ZnS pressure for different values of the compressibility factor

these results fit rather well with the vapor pressure data available for low temperatures and pressures.

7.3. Temperature, pressure and composition in the rocket chamber for Zn/S 2/1

When zinc and sulfur are used under stoichiometric conditions, in principle only ZnS will be produced by the reaction. ZnS will appear under two modifications i.e. solid and gas. The pressure, the temperature and the enthalpy of the products in the motor determine the amount of each phase.

In general, however, there will also be an **equilibrium** between gaseous zinc, sulfur and zinc sulfide:



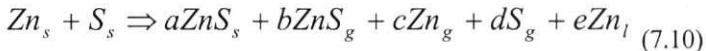
and between :



The dissociation equilibrium of ZnS_g is governed by:

$$K_{ZnS} = \frac{P_{ZnS}}{P_{Zn} P_S} \quad (7.9)$$

The equilibrium between all possible products: their respective equilibrium pressure governs ZnSg, ZnSs, Zng and Zns. In fact the reaction between one mole zinc and one mole sulfur will yield:



Assume now that we only produce ZnS (so no dissociation) and that "x" is the **solid mass fraction**, than "1-x" is the gas mass fraction. The heat content of the material in the chamber per mole at the temperature T°K will be:

$$H = \int_{298}^T Cps. dT + (1-x)\Delta H_s^T \quad (7.11)$$

where ΔH is the heat of sublimation.

After integration, and solving the equation for "x" we find:

$$x = \frac{H - 31841 - 8.92T}{-36354 + 3.89 + 0.000475T^2 + 194600T^{-1}} \quad (7.12)$$

When we know the value of H (which is the reaction heat during the first moments), we can calculate "x" as a function of temperature (and pressure because of the unique relation between temperature and pressure).

7.3.1. The case of hot cast zinc-sulfur rockets

In the case of hot cast zinc-sulfur rockets, the nozzle throat area determines pressure. The smaller the area, the higher the pressure, depending upon the burning rate of the propellant. So when the throat area is fixed, the pressure is also fixed and consequently the temperature is fixed.

The only unknown is the enthalpy H. In this case, however, H is nothing else but the heat of reaction H_R . So in this case "x" is fixed by the choice of the nozzle throat area.

7.3.2. The isentropic expansion in the rocket chamber.

The case of powdered zinc-sulfur, the situation is quite different from hot cast zinc-sulfur propellants. Once the propellant is ignited and the chemical reaction is complete, ZnS undergoes an isentropic expansion in the reaction chamber. This means that the heat exchange with the wall can be neglected, and the physical changes (sublimation) occur in a reversible way (which is not necessarily the case).

The entropy for a gas as a function of temperature and pressure is:

$$S_g^{T,P} = S_o + \int_{298}^{1458} \frac{Cp_s}{T} dT + \frac{\Delta H^{1458}}{1458} + \int_{1458}^T \frac{Cp_g}{T} dT - \int_{P_o}^P \frac{R}{P} dP \quad (7.13)$$

In this formula, S_g is the entropy (in cal/mole°K) at the reference state (T_o , P_o), ΔH is the enthalpy needed to change the state of the material (in our case: sublimation enthalpy). For ZnS_g this will become ($S_o = 13,8$ cal/mole; $T_o=298^\circ K$; $Cp = 8.92$ cal/mole°K, P_o is the equilibrium pressure at $14580K$ which is 1 bar), with P expressed in bar ($R=1,98$ cal/mole):

$$S_{g(ZnS)}^{T,P} = 53.35 + 8.92 \ln \frac{T}{298} - R \ln P \quad (7.14)$$

For the solid fraction, this reduces to:

$$S_s^T = S_o + \int_{T_o}^T \frac{Cps}{T} dT \quad (7.15)$$

or

$$S_{s(ZnS)}^T = 13.8 + 12.81 \ln \frac{T}{T_o} + 0.00095 + \frac{194600}{2} [T^{-2} - T_o^{-2}] \quad (7.16)$$

The entropy in the reaction chamber will be:

$$S_{c(ZnS)}^{T,P} = (1-x)S_{g(ZnS)}^{T,P} + xS_{s(ZnS)}^T \quad (7.17)$$

When the temperature and the pressure have dropped to T_e and P_e , the entropy equation will be:

$$S_{c(ZnS)}^{Te,Pe} = (1-x_e)S_{g(ZnS)}^{Te,Pe} + x_e S_{s(ZnS)}^{Te} \quad (7.18)$$

Since we have stated that the entropy in the chamber does not change, i.e. is isentropic, both entropies must be the same:

$$S_c^{T_e, P_e} = S_c^{T_e, P_e} \quad (7.19)$$

This holds for any combination of T_e and P_e .

From this we can calculate " x_e ":

$$x_e = \frac{(1 - x_e)S_g^e + x_e S_s^e - S_g^e}{S_s^e - S_g^e} \quad (7.20)$$

So if we know the values of x_e , T_e and P_e , we can calculate x_e when the temperature and pressure have dropped to T_e and P_e .

7.3.3. Powdered zinc-sulfur propellants - Zn/S :2/1

In this case, the enthalpy is no longer the reaction heat H_R , since when the reaction between zinc and sulfur is finished, the material in the rocket chamber will expand due to the flow of mass through the nozzle. The fluid expands and consequently the enthalpy will drop. The enthalpy will be a function of the amount of material already released.

The density in the rocket chamber at any moment can be expressed by:

$$\rho_c = \frac{1}{\frac{x_e}{\rho_{ZnS}} + \frac{(1 - x_e)0.08205 \cdot T_c}{Mw_{ZnS} \cdot P_c}} \quad (7.21)$$

In this formula, ρ_{ZnS} is the density of solid ZnS, or 4000 kg/m^3 , Mw_{ZnS} is the molecular weight of ZnS or 97.43 g/mole . P_c is expressed in bar and hence the universal gas constant is 0.08205 .

Because of the relation between the pressure and the temperature, this is a relation between T , x and the density ρ in the chamber.

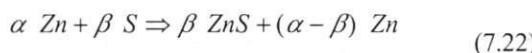
When the rocket is ignited, we know the value of the density (= the total propellant mass divided by the volume of the rocket chamber), and since at that moment the enthalpy H is nothing else but the heat of reaction, we can adopt the expression for x from (7.12). So we have two relations expressing x versus T . The solution yields the values of x and T after the reaction has been completed: (x_e, T_e) .

Using the isentropic equation, we can calculate x_e for any other temperature T_e and pressure P_e . When we put these numbers for T_e and P_e in the density equation, we can find the density in the rocket chamber after any pressure or temperature drop.

To give a complete picture of the situation in the rocket chamber at any time, we still need to know the mass flow through the nozzle as a function of the chamber conditions.

7.4. Temperature, pressure and composition in the rocket chamber: Zn/S 3/1

When zinc and sulfur are used in a ratio larger than 2/1 then there will be an excess of Zn after the reaction has completed. For one kilogram of propellant, the reaction can be written as:



with:

$$1000 = M_w_{\text{Zn}}\alpha + M_w_{\text{S}}\beta \quad (7.23)$$

This means that $(\alpha - \beta)$ mole Zn does not react.

The heat of reaction of this propellant is nothing else but the heat of reaction of β moles of Zn and β moles of S. We know that when we have 1 mole of each, the heat of reaction is 38700 cal/mole (taking into account the fact that 10% is lost). Consequently, for β moles, the heat of reaction will be β times more. So for this propellant composition we will have:

$$H_R = \beta \cdot H_{R(\text{ZnS})} \quad (7.24)$$

If "X" is the fraction of solid ZnS, then $(1-X)$ is the gas fraction of ZnS. For Zn we define "Y" as the liquid fraction, and $(1-Y)$ as the gas fraction.

The enthalpy of ZnS as a function of temperature for one kilogram of propellant is:

$$H_{\text{ZnS}} = \beta \left[\int_{298}^T C_p_{s(\text{ZnS})} dT + (1-X) \Delta H_{s(\text{ZnS})}^T \right] \quad (7.25)$$

or

$$H_{\text{ZnS}} = \beta [12.81T + 0.000475T^2 + 194600 / T - 4513] + \beta(1-X) \Delta H_{s(\text{ZnS})}^T \quad (7.28)$$

For zinc we find:

$$H_{Zn} = (\alpha - \beta) \left[\int_{298}^T Cp_{s(Zn)} dT + 1595 + \int_{692.4}^T Cp_{l(Zn)} dT + (1-Y)\Delta H_{v(Zn)}^T \right] \quad (7.27)$$

With:

$$Cps(Zn) = 5.25 + 0.0027 T \text{ cal/mole} \quad \text{and}$$

$$\int_{T_o}^T Cp_{s(Zn)} dT = 5.25(T - T_o) + 0.0027(T^2 - T_o^2)/2$$

$$Cpl(Zn) = 7.59 + 0.00055 T \text{ cal/mole} \quad \text{and}$$

$$\int_{T_o}^T Cp_{l(Zn)} dT = 7.59(T - T_o) + 0.00055(T^2 - T_o^2)/2$$

692.4°K is the melting point of Zn

$$H_{Zn} = (\alpha - \beta) [4192.92 + 7.59T + 0.000275T^2 - 3309.96] + (\alpha - \beta)(1-Y)\Delta H_{v(Zn)}^T \quad (7.28)$$

$\Delta H_{v(Zn)}^T$ is the vaporization heat per mole Zn (see also next page):

$$\Delta H_{v(Zn)}^T = 30903.17 - 2.62T - 0.000275T^2 \quad (7.29)$$

The total enthalpy per kilogram is the sum of both values:

$$H = H_{ZnS} + H_{Zn} \quad (7.30)$$

This is one equation with 3 unknowns (X, Y, T). To solve the equation we still have to find at least 2 equations.

7.4.1. The vapor pressure of zinc

To establish the vapor pressure of zinc as a function of temperature, we first have to determine the heat of vaporization as a function of temperature.

Two methods can be used to produce gaseous zinc (see figure. 7.3):



Fig. 7.3. Two possible ways to produce zinc gas at temperature $T^{\circ}\text{K}$, starting from solid zinc at 298°K

When we follow the first road (green road): solid zinc is evaporated at 298°K from the solid state and than heated to a temperature of $T^{\circ}\text{K}$. 31190 cal/mole is needed for the evaporation.

When we take the second road (blue), we first have to heat the solid to its melting point (692.4°K), melt it, and heat it further till the desired temperature $T^{\circ}\text{K}$ where it evaporates.

The enthalpy by both ways must be the same:

road 1:

$$H_{g(\text{Zn})}^T = 31190 + \int_{298}^T Cp_{g(\text{Zn})} dT \quad (7.31)$$

with $Cp_{g(\text{Zn})} = 4.97 \text{ cal/mole}$

road 2:

$$H_{g(\text{Zn})}^T = \int_{298}^{692.4} Cp_{s(\text{Zn})} dT + 1595 + \int_{692.4}^T Cp_{l(\text{Zn})} dT + H_{v(\text{Zn})}^T \quad (7.32)$$

From this the evaporation heat becomes:

$$H_{v(\text{Zn})}^T = 30903.17 - 2.62T - 0.000275T^2 \quad (7.33)$$

It is known from zinc that the heat to vaporize it at 1180°K , is 27430 cal/mole. When we apply this formula we find the same value.

The vapor pressure can be found with Clapeyron's law. After integration and knowing that $P=1 \text{ bar}$ at 1180°K , we find:

$$P_{Zn} = \exp \frac{1}{z_{Zn}} (13.39 - 15607.66/T - 1.32 \ln \frac{T}{1180} - 0.000139T) \quad (7.34)$$

The literature also gives a formula for the vapor pressure of zinc:

$$\log_{10} P = (-0.2185 \frac{A}{K}) + B \quad (7.35)$$

A and B are given as a function of the temperature ranges:

A	B	Range °C
30969	8,979	211-405
31787,8	9,2	250-419,4
28181,1	8,105	487-907
28202,7	B,108	600-985
27896,9	8,0726	970-1290

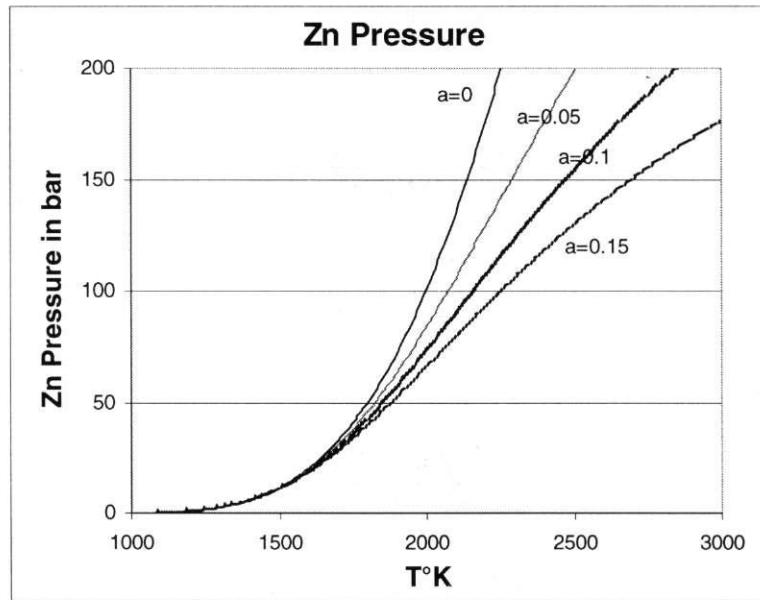


Figure 7.4. Zinc pressure for different values of the compressibility factor z_{zn}

The compressibility factor z_{Zn} as already mentioned for ZnS, is generally a function of pressure and temperature and is positive for large values of the temperature. In our calculations we have adopted the formula:

$$z_{zn} = 1 + a / 100 * P_{zn} \quad (7.36)$$

with the following values for a: 0 (ideal gas) ; 0.05 ; 0.10 ; 0.15

7.4.2. Second equation between X,Y en T

The pressure in the motor is the sum of the partial pressures of zinc and zinc sulfide:

$$P = P_{zn}^T + P_{ZnS}^T \quad (7.37)$$

The partial pressure of zinc and zinc sulfide can also be written as:

$$P_{zn}^T = \gamma_{zn} P \quad (7.38)$$

$$P_{ZnS}^T = \gamma_{ZnS} P \quad (7.39)$$

The mole fractions can be expressed as a function of X and Y:

$$\gamma_{zn} = \frac{(\alpha - \beta)(1 - Y)}{(\alpha - \beta)(1 - Y) + \beta(1 - X)} \quad (7.40)$$

$$\gamma_{ZnS} = \frac{\beta(1 - X)}{(\alpha - \beta)(1 - Y) + \beta(1 - X)} \quad (7.41)$$

When we divide the one by the other, we get:

$$\frac{P_{zn}^T}{P_{ZnS}^T} = \frac{(\alpha - \beta)(1 - Y)}{\beta(1 - X)} \quad (7.42)$$

This expression holds as long as there is liquid or solid zinc. If not Y=0.

7.4.3. Hot cast zinc and sulfur : 3/1

The enthalpy equation for this propellant composition can be written as:

$$H = H_{ZnS} + H_{zn}$$

$$H = A(T) + Xf(T) + Yg(T) \quad (7.43)$$

with:

$$\begin{aligned} A(T) &= \beta(12.81T + 0.000475T^2 + 194600 / T - 4513) + \beta\Delta H_{s(ZnS)}^T + (\alpha - \beta)4192.93 + \\ &(\alpha - \beta)(7.59T + 0.000275T^2 - 3309.96) + (\alpha - \beta)\Delta H_{v(Zn)}^T \\ f(T) &= -\beta\Delta H_{s(ZnS)}^T \\ g(T) &= -(\alpha - \beta)\Delta H_{v(Zn)}^T \end{aligned}$$

The second equation yields:

$$Y = 1 - K(T) + XK(T) \quad (7.44)$$

with

$$K(T) = \frac{1 - Y}{1 - X} = \frac{\beta P_{Zn}}{(\alpha - \beta)P_{ZnS}} \quad (7.45)$$

Putting this expression into the enthalpy equation, we get:

$$H - A(T) = Xf(T) + \{1 - K(T) + XK(T)\} g(T) \quad (7.46)$$

From expression we can calculate X:

$$X = \frac{H - A(T) - g(T) + K(T).g(T)}{f(T) + K(T).g(T)} \quad (7.47)$$

Since in the case of hot cast zinc-sulfur propellants the throat area of the nozzle determines the pressure, and since temperature is determined when pressure is determined, we can calculate X when the enthalpy is known. However in this case the enthalpy is nothing else but the reaction heat.

As long as zinc and zinc sulfide appears in the solid phase, we can make use of the equilibrium equations. In that case, the pressure is the sum of the vapor pressures of zinc and zinc sulfide:

$$P = P_{Zn}^T + P_{ZnS}^T$$

However, when one of the components is completely vaporized, we can no longer make use of the equilibrium equation!!! Since this will happen with zinc first, we have to put in $Y = 0$

$$\frac{1 - Y}{1 - X} = K(T) \quad (7.48)$$

So the equation than becomes

$$X = 1 - \frac{1}{K(T)} \quad (\text{if } Y=0 !) \quad (7.49)$$

Since ZnS remains solid, there is still an equilibrium between ZnS_g and ZnS_s . The vapor pressure can be found by:

$$P_{\text{Zn}} = \frac{(\alpha - \beta)P_{\text{ZnS}}^T}{\beta(1 - X)} \quad (7.50)$$

7.4. 4. Zinc -sulfur powder: 3/1

As in the case of the 2/1 propellant ratio, we will use the propellant density to find a third equation.

For the gas we can write:

$$P = \frac{zRT}{V}$$

In our case this becomes:

$$P = \frac{(z_{\text{zn}}n_{\text{zn}} + z_{\text{zns}}n_{\text{zns}})RT}{V}$$

with: $n_{\text{zn}} = (\alpha - \beta)(1 - Y)$
 $n_{\text{zns}} = \beta(1 - X)$

The total pressure than becomes:

$$P = \frac{z_{\text{zn}}(\alpha - \beta)(1 - Y) + z_{\text{zns}}\beta(1 - X)}{V} RT \quad (7.51)$$

The volume occupied by 1 kg of propellant = $1/\rho_b$ in m^3 . ρ_b is the propellant density in kg/m^3 . When the propellant does not occupy the whole chamber volume ρ_b must be corrected accordingly.

The volume occupied by liquid zinc and solid zinc sulfide:

$$V_{Zn_l} = \frac{(\alpha - \beta)YM_{w(Zn)}}{1000\rho_{Zn_l}} \quad (7.52)$$

$$V_{ZnS_s} = \frac{\beta XM_{w(ZnS)}}{1000\rho_{ZnS_s}} \quad (7.53)$$

The gas volume V in m³ becomes:

$$V = \frac{1}{\rho_b} - V_{Zn} - V_{ZnS}$$

When we fill in the values for the different parameters we get:

$$P = \frac{z_{zn}(\alpha - \beta)(1 - Y) + z_{zns}\beta(1 - X)}{\frac{1}{\rho_b} - \frac{\beta XM_{w(ZnS)}}{1000\rho_{ZnS_s}} - \frac{(\alpha - \beta)YM_{w(Zn)}}{1000\rho_{Zn_l}}} 0.08205T \quad (7.54)$$

Since we know that at ignition the enthalpy is equal to the heat of reaction, the enthalpy equation, taken with the second and third equation yields X,Y and T at ignition.

This knowledge is however not sufficient to describe the conditions in the rocket chamber over time. As in the case of 2/1 we still need the isentropic equation. This will now be derived.

7.4.5. The isentropic equation for 3/1.

We already know the entropies for solid and gaseous ZnS as a function of temperature. We will now derive them for liquid zinc and gaseous zinc.

$$S_{g(Zn)}^{T,P} = 9.95 + \int_{298}^{692.4} \frac{Cp_s(Zn)dT}{T} + \frac{1594}{692.4} + \int_{692.4}^{1180} \frac{Cp_l(Zn)dT}{T} + \frac{27430}{1180} + \int_{1180}^T \frac{Cp_g(Zn)dT}{T} - \int_{P_0}^P \frac{R}{P} dP \quad (7.55)$$

$$S_{l(Zn)}^{T,P} = 9.95 + \int_{298}^{692.4} \frac{Cp_s(Zn)dT}{T} + \frac{1594}{692.4} + \int_{692.4}^T \frac{Cp_l(Zn)dT}{T} \quad (7.56)$$

In this expression:

$$S_{s(Zn)}^{298} = 9.95$$

$$\Delta H_l = 1595$$

$$\Delta H_g = 27430$$

After some elaboration we get:

$$S_{g(Zn)}^{T,P} = 10.15 + 4.97 \ln T - 1.98 \ln \frac{P}{P_0} \quad (7.57)$$

Po is taken at 1180°K.

$$S_{l(Zn)}^T = -32.28 + 7.59 \ln T + 0.00055T \quad (7.58)$$

For 1 kg of propellant the entropy becomes:

$$S_c^{Tc,Pc} = (\alpha - \beta) \left[(1 - Y_c) S_{g(Zn)}^{Tc,Pc} + Y_c S_{l(Zn)}^{Tc} \right] + \beta \left[(1 - X) S_{g(ZnS)}^{Tc,Pc} + Xc S_{s(ZnS)}^{Tc} \right] \quad (7.59)$$

After the temperature has dropped from T_c to T_e , the pressure changes from P_c to P_e and consequently Y_c becomes Y_e and X_c becomes X_e . The entropy at that moment can be found using the same expression but putting in the new values for T, P, X en Y.

As we already know, the two entropies must be equal.

To find X_e and Y_e we still need another equation linking both. This is nothing else but the so-called second equation: (37)

To calculate X_e and Y_e , the following set of equations should be solved:

$$S_c^{Tc,Pc} = S_e^{Te,Pe} \quad (7.60)$$

$$Y_e = 1 - K(T_e) + X_e K(T_e) \quad (7.61)$$

7.6. Solid mass fraction "x", molecular weight "M" and specific heat ration "y"

To use the formulas that have been derived in chapter 6 on NOZZLE CALCULATIONS, we need the mass fraction of the solids, the molecular weight and the specific heat ratio.

The solid (liquid) mass fraction can be found as follows:

$$x = \frac{Mw_{Zn}(\alpha - \beta)Y + Mw_{ZnS}\beta X}{1000} \quad (7.62)$$

or with the values of the molecular weight of Zn and ZnS:

$$x = 0.2412Y + 0.7588X \quad (7.63)$$

The expression for the specific heat γ is:

$$\gamma = \frac{\beta(1-X)Cp_{g(ZnS)} + (\alpha - \beta)Cp_{g(Zn)}}{\beta(1-X)Cp_{g(ZnS)} + (\alpha - \beta)Cp_{g(Zn)} - 1.98(\beta(1-X) + (\alpha - \beta)(1-Y))} \quad (7.64)$$

For the molecular weight of the gases we will get:

$$Mw = \frac{(1-Y)(\alpha - \beta)Mw_{Zn} + (1-X)\beta Mw_{ZnS}}{(1-Y)(\alpha - \beta) + (1-X)\beta} \quad (7.65)$$

CHAPTER 8

MODELING AND EXPERIMENTAL VERIFICATION

In chapters 6 and 7 of part 3, we laid the basis for calculating zinc-sulfur rocket motors. In this chapter, we will use this information to set up a general model describing the situation in the rocket chamber and the nozzle, and verify our results with experimental data.

8.1. Modeling

The possibility to describe and predict mathematically the behavior of zinc-sulfur rockets is one of the greatest challenges. It is of great importance to understand better how these propellants work and to find out what could be done to improve their performance.

Some time ago we tried to develop computer models to describe the behavior of zinc-sulfur propellants. Unfortunately, many of these models were far from useful. They were mostly based on limiting cases such as "no temperature difference between the gas and the particles", or "gas and particles having the same speed". However, one specific approach unexpectedly looks rather successful: the assumption of a complete isentropic conversion, in the chamber as well as in the nozzle. We will describe the results of this approach in the present chapter.

8.1.1. Steady state conditions

Steady state is the easiest condition, which is the case for a cigarette burner, where the reaction can be considered as constant over the whole duration of the combustion.

This model calculates the situation at any cross section of the nozzle as a function of the conditions in the rocket chamber. At a given propellant configuration, it is the size of the nozzle throat that will dictate the temperature and pressure in the rocket chamber, because it regulates the pressure for a corresponding burning rate.

The results, as discussed below for a 3/1 zinc to sulfur mixture, are represented in figure 8.1.1.

- the *gas velocity (purple) increases extremely rapidly in the region just before and after the nozzle throat*. It reaches the velocity of sound in a cross section of the nozzle that is very close to the smallest cross section area that is the throat. It must be observed that the smallest cross-section for the gas (where the speed of sound is reached) is not necessarily the throat, because the condensed phases also play their role in determining the cross section for the gas.
- it is *only near the throat that we observe severe changes in several parameters, like pressure, temperature and speed*. As can be noticed, the pressure drops drastically just behind the throat (this also means that when measuring certain parameters like pressure, the exact location in relation to the throat is very important).
- The *velocity of the gas at the end of the nozzle* can be quite high and reaches values that can be more than twice as large as the measured exhaust velocity, or *more than 1100 m/s*.
- *some parameters hardly change, like the value of the solid ZnS content (magenta)*. This is not the case for Zn (yellow) that evaporates continuously as pressure and temperature drop in the nozzle. *At the end of the nozzle all zinc is evaporated*.
- As can be observed, the *velocity slip "α"(dark green) quickly decreased* to reach a minimum in the nozzle throat. In the divergent part of the nozzle, the velocity slip rises again to quickly reach a plateau value.
- Our calculations show an *exhaust velocity of about 550 m/s*. This is extremely close to what is measured in practice

The main difficulty with this model is the value of the mass rate. This mass rate is very sensitive to the slip in the throat, which depends upon the friction between the gas and solid particles. For the mass flow to be in range with what is measured in actual rocket tests, the *velocity slip α in the nozzle throat must be in the order of 0.02! (meaning that the velocity of solid particles is only 2% of the gas stream)*. This is a remarkably low figure. The mass rate calculation is based upon chamber pressure and the exchange of impulse with the particles. This exchange is very difficult to estimate. In the present model, the solids are considered spherical particles of a given diameter on which the gas exerts a drag. To become mass rate results in our calculation in accordance with reality, we have to consider *very large particles and very low drag coefficients*. Very large

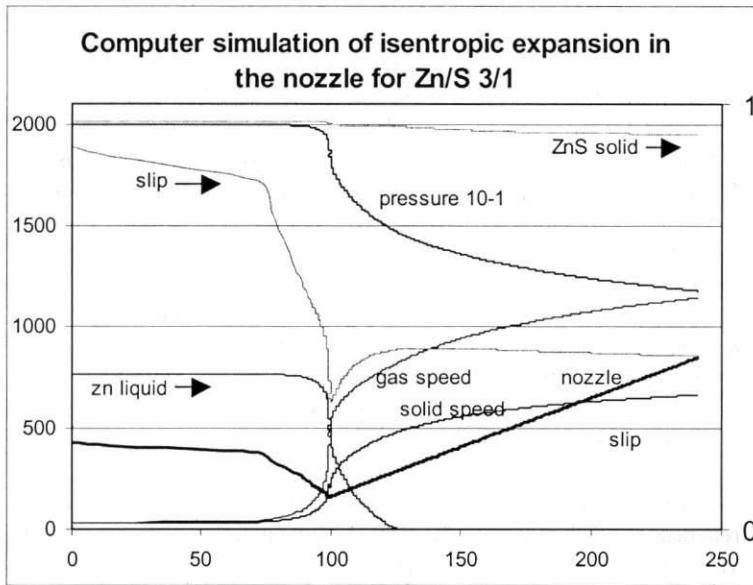


Figure 8.1.1. computer simulation of isentropic expansion in Zn/ S : 3/1 motors

particles, however, will create large differences in temperature between the gas and the particle, as the distance for heat transport in the particle is high. This would contradict the isentropic (equilibrium) assumption. Hence, it is possible that another physical model must be used for the mass flow. One could think, for instance, of the flow of gas through channels in the very compact solid mass, as is assumed to happen for the penetration of gases in zinc-sulfur powder.

An analysis of the exhaust velocity calculations for Zn/S 3/1 at different chamber temperatures and pressures reveals an optimum of around 2100°K. This optimum, however, is not very pronounced. It should be noticed that at higher pressures and thus higher temperatures, the pressure at the end of the nozzle is larger than the ambient pressure, which leads to a loss of speed. The same exercise shows that the mass flow through the nozzle decreases as temperature and pressure goes down.

8.2. Conclusions and verifications with experiments

8.2.1. Location of the point where the speed of sound is reached

Looking at the sensitivity of expression (6.11) page 56, we see that the cross section area for the gas A_g is minimal before the throat ($A = A_t$). The reason is that any slight change of the solid particles constant x , the slip factor α and the density of the gases ρ_g after the throat (x and ρ_g must become smaller due to evaporation and expansion, while α is expected to increase because of smaller accelerations) will increase A_g . This is very important because *at minimal cross area for the gas (which is A_g) the speed of gas should be equal to the speed of sound in that gas at that location*. So the gas reaches the speed of sound at a location which is situated slightly before the throat of the nozzle. The distance may be very small, however, as the cross-area changes rapidly.

8.2.2. Gas speed at the nozzle entrance

With the help of the expression for mass flow (6.12 page 56) we can derive interesting conclusions from experimental data. We shall take the case of the OIR 112 from NERO, for which we have pressure measurements for the chamber and the nozzle as well as a thrust measurement.

Maximum thrust:

- $F \geq 2000 \text{ N}$
- $F/A_t \geq 13275185 \text{ N/m}^2$
- $u_e = 434 \text{ m/s}$

- mass rate $m = F/u_e \geq 4.6 \text{ kg/s}$

u_e is not known at any single moment, but if we take the measured u_e for the whole range of the thrust trajectory we will be close.

The pressure at the entrance of the nozzle is measured at about 90 bar. With a supposed temperature of about 2000°K, this will give us a density for the zinc gases of 39 kg/m^3 and for the ZnS gases of 58 kg/m^3 . Or about 50 kg/m^3 when mixed. The solids have a mean density of about 5500 kg/m^3 .

At the nozzle entrance the area is $A_c = .0045 \text{ m}^2$. This leads to the following value for $m/(A_c \cdot \rho_s)$ = 0.186. This value must equal the following expression:

$$0.186 = \frac{u_e}{\frac{x}{\alpha} + (1 - x_c) \frac{\rho_s}{\rho_g}}$$

In this formula we should have written u_{gc} instead of u_e , but since at the entrance of the nozzle $\alpha \approx 1$, because of the very low accelerations, the two values are almost

equal. Taking also into account that $\frac{\rho_s}{\rho_g} \approx 110$, we find the following relation between u_{gt} and x :

$$u_c = 20.5(1 - x_c)$$

Since we know that x_c is larger than 0.95 at ignition (because all the propellant is still in the chamber), u_c must be in the order of 1 m/s.

8.2.3. Situation at the nozzle throat

In the above-mentioned case, the pressure measurement shows a value of about 35 bar. However this was not taken exactly at the nozzle but at an intersection of 0.000254 m² instead of .00015 m². At an estimated temperature of about 1700°K, this leads to a mean gas density of about 23 kg/m³. We now have a value for $m/(\Lambda * p_s) = 3.29$ kg/s m². Taking into account a value of $\frac{\rho_s}{\rho_g} \approx 239$, we have to fulfil the following expression:

$$m = 3.29 = \frac{u_{gt}}{\frac{x_t}{\alpha} + (1 - x_t)239}$$

Because we have past the minimal cross section, the gas velocity must be somewhat larger than the speed of sound. We assume a value of 400 m/s. So the relation between α and x now becomes:

$$\frac{x_t}{\alpha} + (1 - x_t)239 = 121$$

When we try to satisfy this relation we find that x is larger than 0.5 for any value of α . From this we can conclude that **in the throat, the solid content is (probably much) larger than 0.5 (as confirmed in the model). Corresponding values of α must be very low**. As we do not expect x to be smaller than 0.7, α is expected to be smaller than 0.015. This confirms our conclusions from the model. The velocity of the particles in the throat would then be lower than 27 m/s!

9.2.4. Situation at the nozzle outlet

At the nozzle outlet $\Lambda e = 0.0042$ m²

We assume the temperature to be at the sublimation point of ZnS: 1458°K. We also assume the pressure to be 1 bar. We then get $\rho_g = 0.74$ kg/m³.

$$\dot{m}/(A^* \rho_s) = 0.2$$

Since we have a mean value for the exhaust velocity of the mixture, which is equal to 434 m/s, we now have to satisfy the following relation:

$$0.2 = \frac{434}{(1 - x_c + \alpha x_c)(\frac{x}{\alpha} + (1 - x_c)7432)}$$

This expression teaches us that $0.24 < x_e < 0.42$ for $1 > \alpha > 0$. At the lower boundary for x_e , gas and particles have the same velocity, at the higher boundary the particles would have no speed. So we can conclude that the solid particle content at the end of the nozzle must lay between these two values. This is only possible when all zinc is vapor and a large part of ZnS has also evaporated. This conclusion is not in agreement with the model that predicts a high value of the condensed particle content (around 68%).

THERMODYNAMIC DATA

CHARACTERISTICS	Al	Al ₂ S ₃	S	Zn	ZnS
Melting point °C	660.2	1100	112.8	419.4	1850 at 150 Atm
Boiling point °C	2467	sublimation 1500	444.6	907	sublimation 1185 (1458°C)
Density g/cm ³ (solid)	2.702	2.02	2.07 (20°C)	7.14 (25°C)	3.98 (wurtzite) 41,087 (alpha) 4,087 (alpha) 4.102 (beta) 4.04 (blende)
Density liquid	-	-	-	6.92 (420°C)	-
Molecular weight	26.9815	150.16	32.064	65.38	97.43
Heat of formation kcal/mole	0	-121.6	0	0 (solid 298°K)	(solid to ZnS 298°C) -45.3(sphalerite) - 48,5(wurtzite) - 49,23(blende) -46.04 (wurtzite) - 44,20 (blende)
Heat of formation kcal/mole	-	-	53.25 (gas)	31.245 (liquid 420°K)	to gaseous ZnS (298°K) -14,00
Entropy cal/mole °K .	39.309 (gas)	23	40.085 (gas)	9.95 (solid) 38.45 (gas)	13,8 (sphalerite)
Heat of sublimation/vapor ization kcal/mole	75 (gas)	-	53.25	27.43 27.560	64.30 at 1185°C
Entropy increase cal/mole °K, for sublimation	39.303	-		23.24 (gas)	57.1 (sublimation) at 854°C
GIBBS free energy cal/mole	-	-	-	0 (solid) 22.748 (gas)	-48.11 (blende)

UNDERSTANDING ZINC AND SULFUR PROPELLANTS

EDITION 2001

CHARACTERISTIC	Al	Al₂S₃	S	Zn	ZnS
Free energy cal/mole	-	-	-	0	- 44.20
Specific heat cal/mole°K	4.94 + 2.96 (solid) 7.0 (liquid)	-	3.58+6.24*10^-3 (alpha) 3.56+6.95*10^-3 (beta) 5.4+5.0 *10^-3(liquid) 4.25 + 0.15*10^-3/T - 0.1*10^5/T ² (gas)	5.25 + 0.0027 T (solid) 7.59 +0.00055 T (liquid) 4.968 (gas)	12.81 + 0.00095T - 194600 T ⁻² (solid)
Vapour pressure	Log P= (-.2185* 64257.3 /°K) + 9.052468 724<T°C<1279 (P in Torr) Log P= (-0.2185*62012.1 /°K) +8.701508 1284<T°C<2056 (P in Torr) Log P=(-0.2185* 70859.7 /°K) + 8.549315 1540<T°C<3530 (P in Torr)	-	Log P= (-0.2185* 16609.6/°K) +8.015165 182<T°C<444 Log P= (-0.2185* 15377.8/°K) +7.559047 445<T°C<720	Log P=12.448-1.2742 logT- 6674.4T ⁻¹ (liquid) 764>T°K>1254 Log P=-7198*T ⁻¹ + 9.664 (solid) 300<T°K<700	log P = 148.63 T ⁻¹ + 20.37 log T-63.84(P in atm) 900<T°K<1250 Log P= -13.981T ⁻¹ +8.979
Heat of fusion kcal/mole	2.57 (liquid) 67.9 (gas)	-	0.088 (beta) 0.293 (liquid) 2.5 (gas)	1.595 1.765	-

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