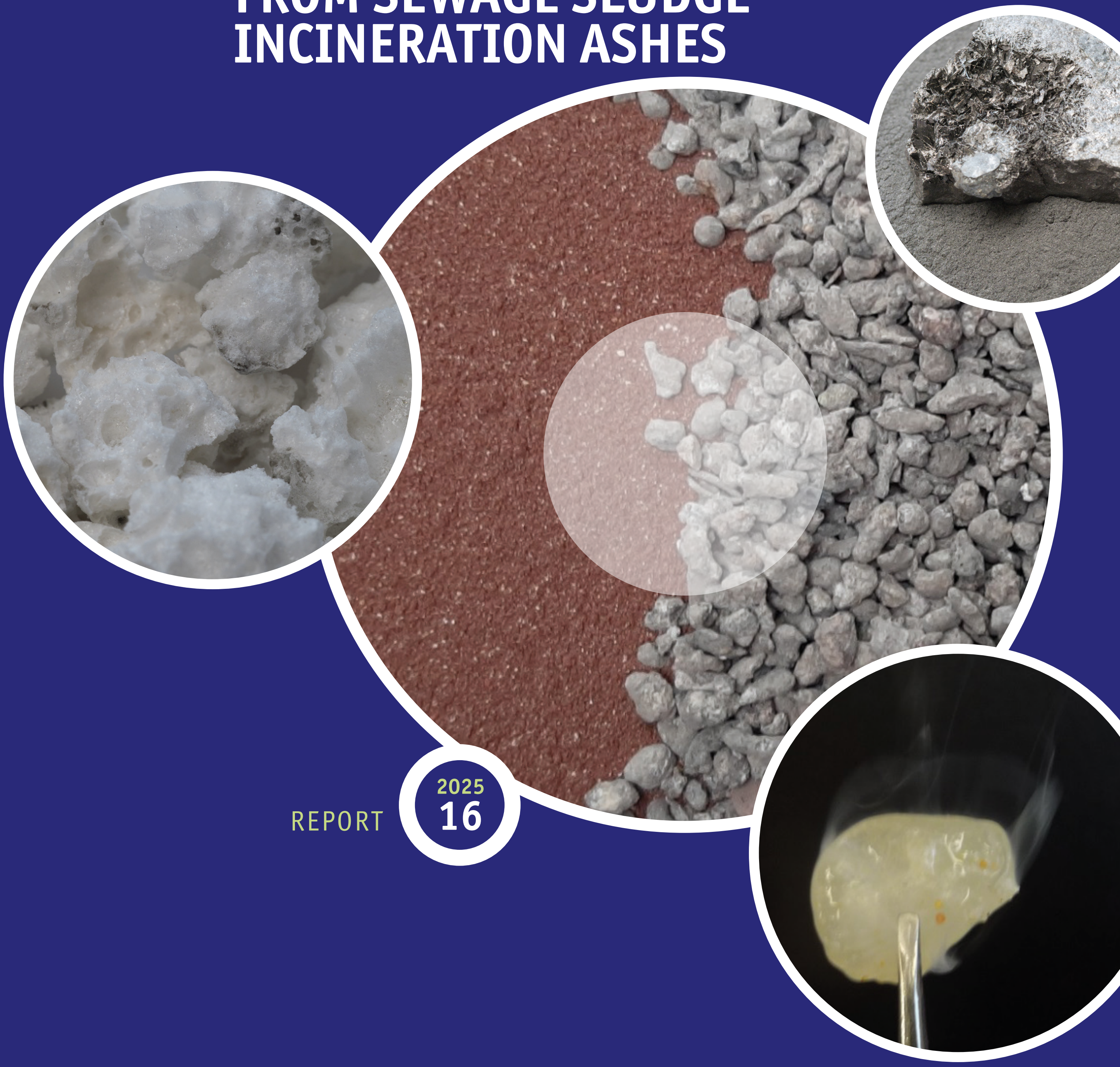
QUALITY AND APPLICATIONS OF THE PRODUCTS AND UPDATE ON ECONOMIC FEASIBILITY AND THE LCA

SPODOFOS:

WHITE PHOSPHORUS PRODUCTION FROM SEWAGE SLUDGE INCINERATION ASHES



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FOREWORD

IMPROVED PROSPECTS FOR PHOSPHORUS RECOVERY

Dutch water boards have set themselves high sustainability goals ("Het verhaal van de Circulaire Waterschappen", Union of Water Boards, 2021). Due to the finite nature of phosphate, recovery of this important raw material is one of the ambitions. In fact, a significant part of national phosphate consumption flows through wastewater treatment plants and must be removed. The new EU Urban Wastewater Treatment Directive (2024) anticipates on mandatory recovery of phosphate from the water treatment chain.

It is generally stated that effective large-scale recovery of phosphate is most efficient via incineration ash of sewage sludge. This enables circularity of phosphates by processing the ash into a fertiliser. Most technologies for large-scale recovery from ash are based on acid leaching of the phosphate. No commercial plant is currently in operation, but several international initiatives are underway. A general challenge is to make recovery economically attractive and commercially robust.

The Spodofos process is an entirely different approach to the recycling issue, employing thermal methods to recover phosphorus from sewage sludge ashes. The feasibility study (STOWA 2021-57) concluded that the prospects of this recovery method could be very good. The level of development was still low at that time, but great progress has been made since. With this follow-up study, the circularity aspects of Spodofos are investigated through field tests and expert assessment.

The results are better than the expectations in the feasibility study. Spodofos is a process that produces white phosphorus, a mineral slag and an iron alloy. The iron alloy and slag exhibit special properties and can replace high-value primary products. The heavy metals in the sewage sludge ash are captured or immobilised. The white phosphorus can be sold as a sustainable and circular product. Because all Spodofos products are intended as replacements for energy-intensive primary products, the LCA points to strong carbon negativity.

Due to its high-value applications and negative carbon footprint, established market players are already showing interest in off-taking these Spodofos products. A great advantage to further development is the existing involvement of market players in this stage of the project.

This route can make an important contribution to the water boards' sustainability goals. Next development steps will be followed with interest.

Mark van der Werf
Director STOWA

SUMMARY

In the Netherlands and abroad, there are many initiatives to recover phosphate present in wastewater. This is possible at several places in the wastewater treatment and sludge processing chain. At sewage treatment plants, phosphate is mostly recovered as struvite, with the additional benefit of significantly reducing maintenance costs. An important route for large-scale phosphate recovery is from the ashes remaining after the mono-incineration of sewage sludge. A major advantage to this method is that this step of the process is where the concentration of phosphate is highest over the entire sludge processing chain. Also, in terms of input product quantity, this gives recovery the best starting position.

This ash from urban water treatment sludge contains up to 10% phosphorus (or about 25% P_2O_5), and is released in large volumes at a limited number of sites, which makes it an interesting recovery prospect. The most developed techniques for extracting phosphate from sludge ash are based on acid leaching, producing a crude phosphoric acid solution that is further processed into a feedstock for fertiliser production and technical applications.

Publication STOWA 2021-57 [1] reported the feasibility of a new process for phosphorus recovery. This so-called Spodofos process is fundamentally very different from all other developments.

In the Spodofos process, some oxides in the sludge ash are reduced with metallic aluminium, producing elemental phosphorus (white phosphorus, P_4). In addition, this thermal process produces a mineral slag and a metal product. The conclusions in this report confirm the process technology's feasibility and show that the process' sustainability and economic feasibility are quite attractive.

As a follow-up to this feasibility study, some chain parties have invested in the further development of Spodofos. From October 2022 to December 2024, TRL (Technology Readiness Level) 4 and 5 have been successfully completed. This means that the pilot phase will be next.

As part of TRL 5 (prototyping specific process equipment), a project has been defined in which the sustainability and economic prospects of Spodofos are further determined based on measurements and expert assessments, with regards to the quality and applications for the process end products. Indeed, in [1], applications based on calculations and expectations were analysed for sustainability and financial feasibility. In TRL 5, products were created under representative conditions and subjected to selected field tests for the purpose of defining applications. With the findings in TRL 4 and 5, the technological feasibility was confirmed in practice.

Successive steps in this study are:

- select potential applications to be tested from the previously mentioned overviews,
- create sufficient products in a representative manner,
- determine the quality of each product and have the application tested in practice and/or assessed by an expert,

- prepare a new process configuration and business case based on the applications with the best prospects,
- perform the LCA analysis on the base case and individual products.

White phosphorus was not tested because it has a guaranteed application as a chemical commodity. Adequate capture of dust, zinc, sodium and potassium from the phosphorus gas stream is still lacking from the test setup in TRL 5. As a result, the quality determining arsenic content in the phosphorus is still unknown, but the calculated maximum is comparable to the arsenic content of phosphorus from conventional phosphorus furnaces. Other quality parameters are expected to be better. Some high purity white phosphorus was produced via distillation.

Spodofos slag is characterised by a high alumina content of about 50%. Quartz and lime each occupy 20 to 25%. This type of slag is not known from other metallurgical processes, making applications unclear beforehand. The slag from the Spodofos reactor is found to contain very little heavy metals: only 30% remains of the amount of chromium originated from the sludge ash. In the feasibility study [1], the slag is applied as a gravel substitute in road foundations. This application is quite feasible because the leaching of the slag meets the standards laid down in soil quality regulations. However, crushed slag does not have a cementing effect, so it does not exhibit slab action in foundations.

The slowly solidified slag has been tested as granulate in refractory concrete, where it could replace high-temperature fired chamotte. After some optimisation in the concrete formulation, a brick has been made of which experts are hopeful.

Tests have been carried out to cast the liquid slag into moulds in order to manufacture pre-shaped building materials or refractory elements. It appears that this is certainly possible, and a strong material is obtained. The test was carried out solely to use the particularly high heat content of the liquid slag as well, and to test this route in the base. It is an option that can be worked out at a later time.

An important aspect regarding slag properties, is the rate of cooling or solidification. The above applications are based on slow cooling creating a vitrified compact stone. When cooling rapidly, in water, expanded slag forms, which is very bulky and amorphous in structure. After grinding, this slag exhibits good cementing properties in the presence of lime (compare fly ash as a cement substitute). About 30% of cement can be replaced by the ground Spodofos slag, while retaining strength. A manufacturer of secondary concrete indicates that, at a good price, it can handle many times the Dutch sludge ash volume. This route for the slag was therefore chosen as the base case.

A second application of expanded slag is as an insulating granulate in refractory products. For this, the slag needs to be slightly crushed, and the resulting product could replace expanded chamotte. The softening temperature is just at the lower limit but could possibly be optimised. The economic value here is extremely high, however, the sales volume is a fraction compared to that as a cement substitute.

For both applications of expanded slag, necessary developments need to be made on the product side. In the Spodofos process, the slag will have to be produced within quality specifications which have to be established.

The metal product from the reactor consists of liquid iron containing dissolved phosphorus and silicon. In all thermal processes, this ferrophosphorus is the determining factor in white phosphorus recovery efficiency. In the resulting ferrophosphorus, the phosphorus content is lower than expected: the phosphorus recovery efficiency in this process is about 90%. It is therefore expected that, after optimisation, the yield will become higher.

Ferrophosphorus is a highly inert and a magnetically sensitive alloy and is extremely brittle. It is easily ground.

Ferrophosphorus from conventional phosphorus furnaces finds its way into the steel industry. The composition of ferrophosphorus from Spodofos proves unsuitable for this purpose. As a substitute for zinc powder in anti-corrosion coatings, the finely ground material does not show sufficient zinc-replacing action.

Given the properties of ferrophosphorus, the material appears to be a good candidate to substitute ferrosilicon used in dense medium separation (DMS): as a suspended medium in water, the suspension can obtain a density of up to more than 3.0, enabling all kinds of separation processes based on density difference. A global firm operating in this market foresees great opportunities for Spodofos ferrophosphorus, in both volume and price. There are no a priori concerns that this route will not be feasible. When ferrophosphorus becomes available in larger quantities, extensive testing will have to be carried out. Because of its high value and easy post-treatment (milling), this application for the ferrophosphorus was chosen in the base case.

A second option for the ferrophosphorus is to convert it into a coagulant (iron(III)chloride, to be used at wastewater treatment plants) and a virtually iron-free phosphate-rich substance that can be fed back to the input of Spodofos. This makes P-recovery efficiency extremely high (>>95%). The downside is that this conversion into coagulant and phosphate product requires many processing steps and chemicals, which reduces the advantageous simplicity of the Spodofos' process. There are also some unanswered questions (e.g. whether a higher copper content in coagulant is permissible). Because of the resulting complexity, this route is retained as a secondary option.

The heavy metals in the sludge ash are distributed among the three product streams. In the slag, 1/3 of chromium remains as the only heavy metal; copper, nickel and residual chromium accumulate in the ferrophosphorus. Around 1/3rd of lead and cadmium are found in the ferrophosphorus. All zinc and arsenic, as well as residual lead and cadmium, leave the reactor with the gaseous phosphorus. Apart from the arsenic, the heavy metals, along with sodium and potassium, will have to be captured.

Due to the immeasurable leaching of slag and ferrophosphorus and the inert properties of both, the products can be expected not to be environmentally hazardous. Because of the high-value applications and expected market demand, end-of-waste status is a real possibility. Per tonne of sludge ash, about 30 kg of material remains to be landfilled unless zinc and alkali metals are found to be recoverable.

The base case in [1] can be further extended with an achievable higher P-recovery efficiency.

In the Spodofos base case, besides white phosphorus, expanded slag and ground ferrophosphorus are the two products. The business case from 2021 [1] has been adjusted with these changes in mind, and includes adjusted prices for energy, chemicals and construction costs, at the same gate fee for the sludge ash (€90). The payback period for a 50 kt plant then drops to under 4 years at an excellent internal rate of return (30%).

The sensitivity of the business case to variations in the market price for aluminium and white phosphorus has been analysed. The outcome is that, even in volatile commodity markets, the business case is robust and improves rather than deteriorates.

The LCA of the Spodofos process was carried out by CE Delft based on the outcomes of the product applications study and the findings in TRL 5. These outcomes were included into the configuration of the proposed Spodofos plant.

An important change in the LCA calculation is the application of the Product Environmental Footprint, a European directive to encourage recycling by partially allocating the CO_2-footprint of primary raw materials to the corresponding secondary raw materials to be recycled. For Spodofos, this means that 39% of the footprint of primary aluminium is allocated to the secondary aluminium from waste incineration. This significantly changes the LCA of Spodofos but also eliminates the discussion on the use of the energy present in the aluminium. Of all the CO_2-eq. input to the process, more than 90% now comes from this allocation.

The emission of the process from a waste perspective is -1.4 metric tonnes of CO_2-eq./tonne of sewage sludge ash. Processing sludge ash via Spodofos is therefore associated with significant reduction of CO_2-eq. emissions. This stems from the fact that all Spodofos products replace primary raw materials, which are all manufactured at very high temperature and using cokes, thus increasing the materials' carbon footprint.

The (avoided) emissions can be further improved when:

- aluminium types are used that are difficult to recycle aluminium as a metal,
- the residual heat recovered from solidifying the slag (-0.12 metric tonnes of CO_2-eq./tonne of ash),
- and pre-heating energy comes from renewable electricity (-0.08 metric tonnes of CO_2-eq./tonne of ash).

The carbon footprint per tonne of sewage sludge ash is the benchmark for a comparison between phosphate recovery technologies. As a comparison, only an LCA is available for a technology based on acid leaching (STOWA 2023-08). The determined climate impact converted to 'per tonne of sewage sludge ash' is slightly positive. Spodofos, with its strongly negative CO_2-eq. emission, is far ahead of this number.

From a product perspective, the percentual reduction in climate impact is at least 44% for white phosphorus and 75% and 69% for slag cement and ferrophosphorus, respectively. These figures make the business case future-proof because sustainable procurement by companies is permanent.

The overall conclusion is that Spodofos has particularly good prospects. With the development level TRL 5 already reached, the feasibility of a fully continuous process is considerably closer. In the pilot, some technical developments are necessary to achieve this. After that, it will be clear whether large-scale processing is feasible.

THE STOWA IN SHORT

HOW WE WORK

STOWA is the knowledge and innovation hub for regional water managers in the Netherlands, serving the water authorities and provinces. We help them gain the insights and knowledge they need to tackle regional water management challenges more effectively. We do that by identifying and prioritizing key research questions through dedicated program committees. We commission our research from a range of experts, consultancies, institutions, and universities, and oversee them in their work.

Once the research is complete, we ensure that the findings are shared widely within the broader water management community. We also promote experience and knowledge sharing through events, working groups, excursions, conferences and communities of practice. We work together with ministries, Rijkswaterstaat, municipalities and water companies, among others.

OUR RESEARCH FOCUS

STOWA's research covers all facets of water management, from flood defense and urban water management to water treatment and systems. Key themes include climate adaptation, flood protection, water quality and ecology, energy transition and circular economy.

The research questions we address span technical disciplines, the natural sciences, governance, legal frameworks and the social sciences. All our work is geared towards providing practical solutions for regional water managers. This is central to our mission as the Foundation for Applied Water Research.

WHO WE ARE

As a knowledge organization, STOWA is independent, impartial and transparent. Users of our knowledge can trust that the findings in our reports are objective and balanced. This ensures that our knowledge provides a reliable foundation for improving water management and fostering innovations to meet today's and future challenges. The regional water managers themselves decide how to apply STOWA's insights in practice. While STOWA can serve as advisor, we do not play a role as implementors or directors.

STOWA is a non-profit foundation and follows the guidelines for non-profit organizations (RJ-640). Our annual report includes both financial statements and a detailed overview of the foundation, its activities and key statistics.

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1

INTRODUCTION

1.1 BACKGROUND

Of all imported phosphate in the Netherlands, about 35% eventually ends up in wastewater treatment plants [2]. There, most of the phosphate is chemically or biologically bound and becomes part of the sewage sludge.

The reuse of phosphate has attracted worldwide attention as the horizon of economically mineable phosphate resources comes into view. Although the ambitions of water boards are clear, to this day there are almost no large-scale phosphate recovery plants. The challenge is to make a phosphate product using an economically feasible method and in sufficiently large volume. An existing market for the P-product, or one that can be easily set up, is crucial for the viability of P-recycling. Small scale installations are being operated to partly remove phosphate at the water treatment plant as struvite to reduce accumulation in piping requiring costly maintenance.

Up to now, phosphate is therefore virtually non-circular and ends up on the ocean floor (if discharged to surface water), in cement (especially as bone meal), or as a filler of asphalt or closed mines (if captured in sewage sludge ash).

Recovery of the element phosphorus from sewage sludge is a major concern for Dutch water boards. The removal of nutrients from sewage water, such as phosphorus, is a core task for sewage treatment plants. In sewage water, phosphorus is present in the form of phosphate and is removed and concentrated in the sewage sludge. After mono-incineration of the sludge, the phosphate is concentrated in the remaining sludge ash. The ash contains about 10% phosphorus (or 25% P_2O_5) and is comparable to low grade phosphate rock. While circularity is rapidly becoming more important, water boards view the recovery of this valuable raw material as a co-objective of their core activities.

There are several options for the recovery from sludge ashes, but the challenges that often come into play are:

- the strong binding of phosphate with the iron typically found in the sludge,
- the presence of heavy metals,
- the beneficial uses of by-products from the P-recovery process,
- economic feasibility of P-recovery.

For economic feasibility, an important factor is how the process works and whether the resulting phosphorus product will become available in sufficient quantities and will be sold at a good, market-based price. There is certainly a drive among phosphate or phosphorus buyers to use secondary phosphate or phosphorus in their products.

The most extensively developed technologies for extraction of phosphate from ash are based on acid leaching, which produces a crude phosphoric acid solution that, after processing, is suitable as feedstock for fertiliser production and for technical phosphoric acid applications.

Other technologies under development are mostly of thermal nature. Without going into too much detail, the main pathways are:

- removal of heavy metals by evaporation as chlorides; the sludge ash becomes a (new) fertiliser,
- reducing iron and some heavy metals; metallic iron and a mineral phosphate fertiliser are created,
- reducing iron and phosphate; metallic iron, low phosphate slag and elemental phosphorus are formed.

The latter principle also applies to Thermphos processing (until 2012) of SNB ash as an additive to phosphate ore. However, in order not to adversely affect the main process and production costs, only sludge ash with low iron content could be used.

Apart from the Thermphos route, thermal technologies have not been developed into commercial plants.

1.2 SPODOFOS

A new thermal technology under development is the Spodofos process. The chemical background of Spodofos is not straightforward and has therefore not been recognised before. It involves the reduction of iron and phosphate in sludge ash to metallic iron and elemental phosphorus with aluminium metal as the reducing agent. The reaction is known as a thermite reaction.

Dutch start-up ThermusP BV focuses on the development of this process.

The Spodofos process was investigated in STOWA study 2021-57 [1] for technological and economic feasibility and sustainability. For details, please refer to the said report which is summarised here:

CHEMICAL BACKGROUND

The reactions to be achieved in Spodofos are (most importantly) the reduction of iron and phosphate with aluminium. Simplified:

$$Fe_2O_3 + 2\ Al \rightarrow 2\ Fe + Al_2O_3$$
$$P_2O_5 + 10/3\ Al \rightarrow P_4 + 5/3\ Al_2O_3$$

Phosphate is generically represented as diphosphorus pentoxide (P_2O_5).

Both reactions produce a lot of heat. With limited preheating of the ash and aluminium, the reaction becomes self-sustaining and external energy can be basically omitted. The aluminium thus acts as both a reductor and an energy carrier. In traditional phosphorus furnaces, these roles are fulfilled by cokes and electricity, respectively.

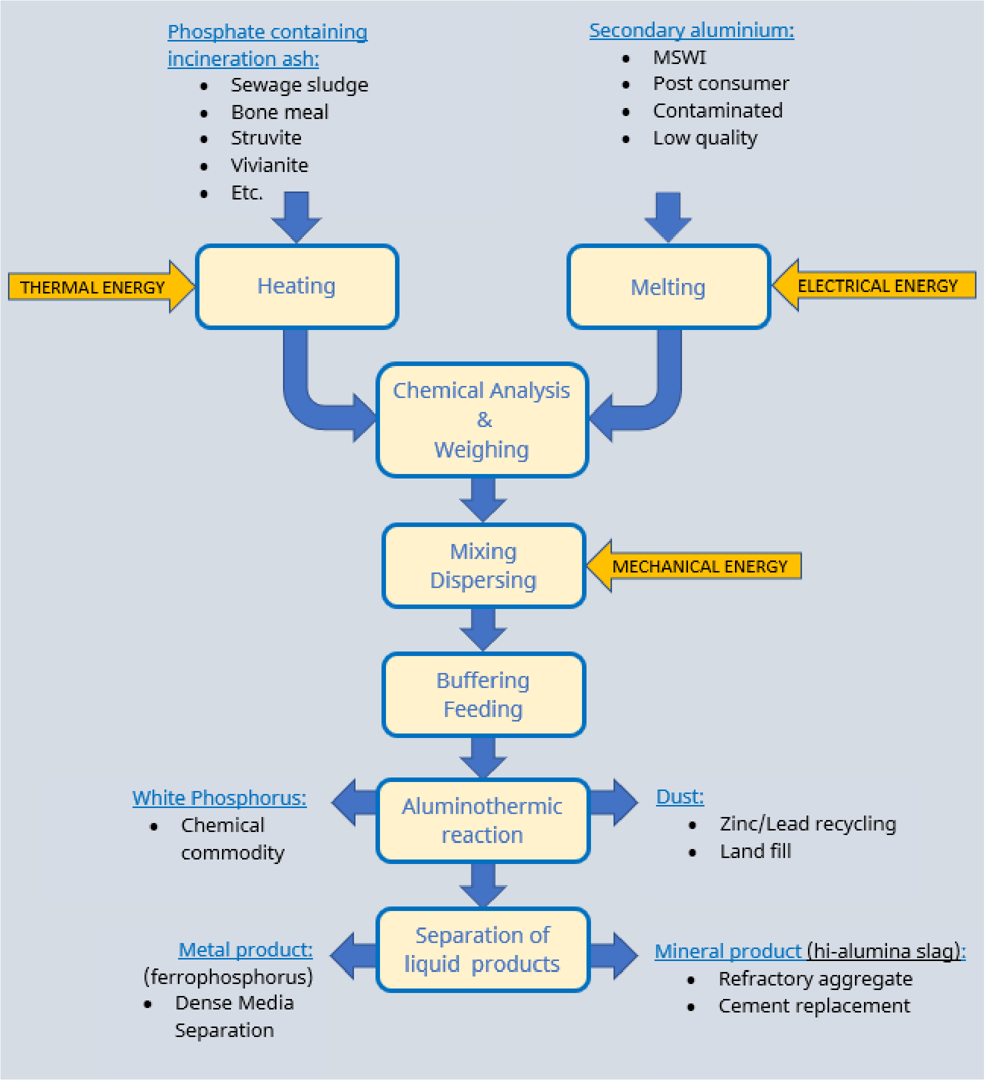
The aluminium to be used can come from the lowest quality scrap, for example from municipal waste incineration.

The temperature in the reactor should be very high (>1,600°C) so that the mineral parts of the ash mixed with the alumina formed are in liquid state. Only then continuous process operation is possible. The high temperature is mainly achieved with the heat of reaction.

The resulting phosphorus (P_4) escapes from the reaction zone as a gas and is condensed by cooling. Because the phosphorus is gaseous as an intermediate phase, an inherent purification step is present and high-quality phosphorus product can be achieved without additional laborious purification.

An unfavourable side reaction is the dissolution of phosphorus in the liquid iron. As sludge ash contains a lot of iron, this determines the efficiency of P-recovery. Compared to traditional phosphorus furnaces, in Spodofos, the higher temperature is more favourable, reducing the loss per part iron. Furthermore, the Spodofos reactor and process control can be designed to increase the phosphorus yield.

FIGURE 1 **SPODOFOS PROCESS DIAGRAM**



PROCESS

A plant of very limited size is required to facilitate the conversion. The largest volumetric throughput is equal to that of the sludge ash and total residence time of the ash in the plant will be in the order of 1 to 2 hours.

The process consists of three steps: preheating of ash and aluminium, conditioning of the reaction mixture, the reaction and separation of slag and iron. The remaining process steps include product collection and processing.

The conditioning of the reaction mixture aims to achieve a homogeneous and reactive mixture. This involves starting the reaction when dosing the mixture to the reactor and ensuring that the reaction fully completes.

A major advantage is that the gas flow from the reactor in Spodofos consists almost entirely of phosphorus gas; in traditional phosphorus production, this comprises only 10 to 15% of the gas flow. The remainder is mainly carbon monoxide. As a result, the reactor feed does not need to be sintered to obtain sufficient gas permeability and to prevent excessive dust entrainment.

PRODUCTS FROM THE PROCESS

Per metric tonne of sludge ash of average Dutch composition, the following quantities of main products will be released: white phosphorus (about 85 kg), slag (about 1,000 kg) and ferrophosphorus (about 120 kg). In addition, some dust and condensed volatile compounds will have to be captured. The considerable heat content of the slag can also be regarded as a product, amounting to ca 2.3 GJ/metric tonne of sludge ash, equivalent to approximately 70 m^3 of natural gas. However, as this heat comes from a solidifying liquid, it is not easy to extract the energy at higher temperatures for reuse.

All products are discussed in detail in chapter 2.

SUSTAINABILITY

The climate impact was calculated by CE-Delft. The result, a negative climate impact per tonne of sludge ash processed implies reduced CO_2-eq. emissions via replacement of energy-intensive primary products with Spodofos products.

These calculations are based on intended application of post-consumer aluminium scrap. But even if primary aluminium is used in calculations, the climate impact remains negative. However, application of primary aluminium is not realistic, since the operational cost would be too high.

The LCA was modified in STOWA 2023-8 (p.64) by attributing all CO_2-eq. to the recovered phosphorus. This implies that slag and ferrophosphorus do not represent climate impact.

In recent years, a new LCA calculation method has become standard for the EU (Product Environmental Footprint). In this method, part of the climate impact of a given primary material is allocated to a recyclable material. This report updates the LCA of Spodofos, based on this new methodology, as described in chapter 7. As a result, the previous calculations are no longer applicable and are not cited here.

BUSINESS CASE

In STOWA 2021-57 [1], multiple business cases were calculated for Dutch sludge ash of standard composition, depending on scale and application of the slag. The gate fee of sludge ash and the aluminium and phosphorus market prices that were used in the business case were the contemporary values. The slag price varies by application, and ferrophosphorus was estimated at a conservative zero value.

Because the process is compact, necessary investments turn out to be very limited. In contrast, because of the full-continuous operation, personnel costs are significant. It is advantageous if Spodofos processing can hook up to an existing 24/7 organisation so that overhead and general facilities can be shared. This possibility has not been included in the calculations.

At this early stage of development, the business case outcome is expressed in terms of simple payback time and internal rate of return (10 years). Based on the reluctant expectations and revenues of the products, excluding phosphorus, a payback period of 5.1 to 7.7 years was calculated, at an initial investment of €5.2M. IRR is estimated to be between 6 and 13%.

In this study the business case is updated (see section 6.2).

DEVELOPMENTS SINCE 2021

Based on the STOWA feasibility study in 2021, chain partners were found who recognised the prospects of Spodofos. With investments, facilities and/or in-kind support, the critical development phases of Spodofos were realised. TRL phases 4 and 5 were further defined and executed with a steering committee consisting of investor representatives. The topics included safety regarding the reactive mixture, the method of conditioning the reactive mixture, operating the reactor, and manufacturing and testing prototypes for the pilot plant.

CONNECTION OF THIS RESEARCH TO THE DEVELOPMENT OF SPODOFOS

This STOWA project involves determining the sustainability and economic feasibility of Spodofos with respect to its end products. In this perspective, the applications of slag and ferrophosphorus are crucial, and the business case has only been calculated on the basis of expectations. By verifying the quality and applications of the end products through field tests and expert assessments, sustainability and economic feasibility will become demonstrable. Furthermore, the mass balance can be established based on measurements. This is important for Spodofos' financial outcome and optimisation. The distribution of heavy metals to different products is also investigated.

Together with the results of technological developments, this research further defines the feasibility of the Spodofos concept.

1.3 STRUCTURE OF THE REPORT

This report comprises the practical research on the quality and applications of the products of the Spodofos concept to complement the initial theoretical evaluation [1].

Up to TRL 3, reaction tests were carried out on a small scale (on the order of tens of grammes) and under suboptimal conditions (large heat losses). In TRL 4 and 5, the technology of conditioning the reactive mixture and operating the reactor were developed. With this knowledge and experience, it has become possible to safely prepare sufficient and representative products for the tests in this study.

Chapter 2 gives an overview of the anticipated and conceivable applications of the products. For each product, a selection is made of the most useful applications that will be tested.

Chapter 3 describes the preparation process and covers mass and component balances.

Chapter 4 describes the execution of the individual application tests and the results. Evaluation will take place in chapter 5.

Chapter 6 describes the Spodofos configuration, with the sales and associated post-treatments of slag and ferrophosphorus, determined through the results this study. The business case is also recalculated.

Chapter 7 discusses the LCA of the process from the perspective of the waste and from the perspective of the selected products.

Conclusions and follow-up research are in the last chapter.

2

APPLICATIONS OF SPODOFOS PRODUCTS AND TEST SELECTION

2.1 INTRODUCTION

This chapter gives an overview in which applications the products may be suitable and what the conditions are for successful ultimately useful applications. On this basis, application tests are selected that are of interest and/or most likely to succeed.

Despite all products originating from waste and therefore in principle being considered waste, they could exhibit non-waste characteristics. A status upgrade to end-of-waste is desirable. This aspect is a next step in the exploration of applications.

2.2 WHITE PHOSPHORUS

White phosphorus is a raw material for the chemical industry. Currently, EU companies import 70% of the phosphorus from Kazakhstan and 30% from Vietnam. This phosphorus is produced from phosphate rock. The production of white phosphorus from only secondary raw materials has not yet been realised. There is widespread interest in circular phosphorus among white phosphorus users, for two reasons:

- to become less dependent on the two supplying countries,
- and to be unique among producers.

The Spodofos route is particularly interesting because the CO_2-footprint of the phosphorus is low compared to other production methods. As a result, it also contributes to the sustainability objectives and public image of the company purchasing the phosphorus.

There is no need to find other applications for secondary white phosphorus, since it can be marketed as a substitute for imported phosphorus. The defining characteristic for white phosphorus value is purity of the material. Impurities may reduce the suitability of the phosphorus for certain applications or even exclude those applications entirely.

Primary white phosphorus (about 99.6% pure) contains impurities from the phosphate rock, the aggregates (including quartz) and from the production method. Typical maximum impurities are given as in Table 1.

TABLE 1 **TYPICAL IMPURITIES OF WHITE PHOSPHORUS (ULLMANN 1979)**

Component	Arsenic	Organics	Lead	Iron	Sulphur	Water
Content ppm	150	500 as C	5	50	500	0.3%

Organic matter comes from the carbon electrodes during primary phosphorus production, mostly as aromatic components from the tar of the electrodes. This contamination limits the number of applications.

Furthermore, metals are becoming increasingly important for the production of 'electronic grade' phosphoric acid for application in the semiconductor industry. This may involve levels at the ppb level.

For phosphorus from Spodofos, the sludge ash and aluminium scrap used are the sources of the contaminants.

Sludge ash, volatile components and/or aluminium can be carried out of the reactor with the phosphorus flow. Adequate dust removal upstream of the phosphorus condenser is necessary, and this is common practice in phosphorus furnaces. In this study, this cleaning step is not yet implemented. Furthermore, volatile components can reach the condenser and thus the phosphorus product. Arsenic can be expected as an impurity at this point. Other potentially volatile components such as cadmium, chlorides, zinc, lead and sulphur should deposit on walls in the relatively cold connecting pipe between reactor and condenser. Entrainment of this dust by the phosphorus gas into the condenser cannot be ruled out in advance.

Alkali metals (sodium, potassium) are present in the ash and can also be considered volatile at the temperature levels in the reactor. If these components reach the condenser, they are expected to dissolve in the circulation water.

At present, the fate of the sulphur in the sludge ash (mostly as sulphate) after the Spodofos reactions is not known. With an additional amount of aluminium, it can be reduced from elemental sulphur to sulphide. Both elemental and reduced sulphur interact with the slag, ferrophosphorus and possibly phosphorus. This needs further defining and optimising.

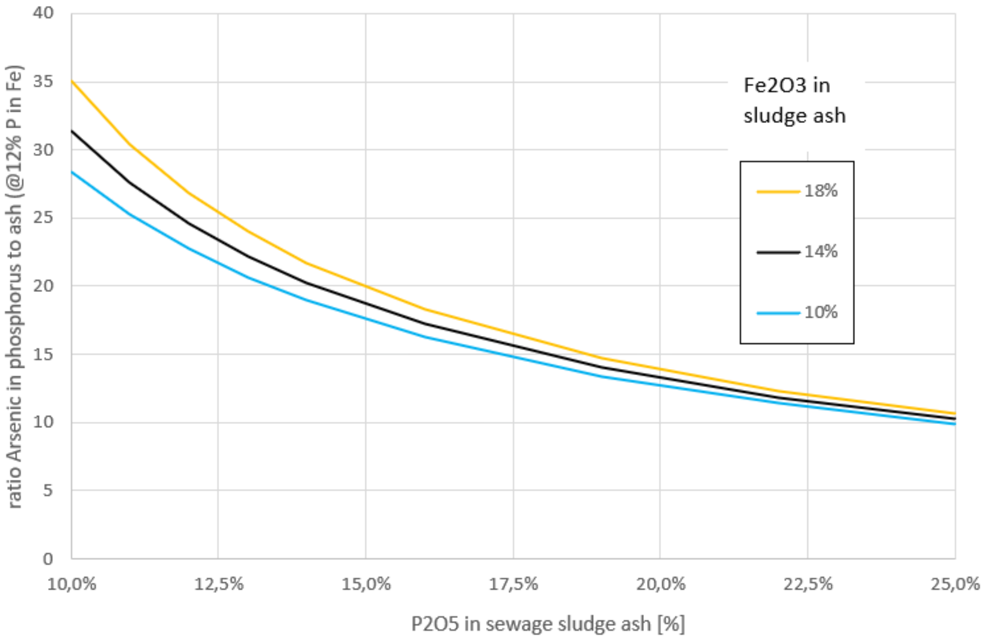
Arsenic is the most characteristic impurity of white phosphorus. Its level can block the production of 'food-grade' phosphoric acid, or the phosphorus must be purified.

For arsenic, a worst-case calculation can be performed with two realistic and one worst-case assumption. Firstly, phosphate to phosphorus conversion is 100%; it has been measured before that more than 99% of phosphate disappears from the mineral fraction. Secondly, ferrophosphorus contains about 12% P (excluding silicon). This content is lower than expected. Optimisation of process operations has not yet been addressed, so an even lower P content seems feasible. In the worst-case scenario, all arsenic ends up in the phosphorus. This is unlikely, but a high percentage is to be expected.

The worst-case, or maximum arsenic content in the phosphorus product can then be calculated from the iron, phosphate and arsenic content in the ash. This is shown in graph 1.

For a specific phosphate and iron content in the sludge ash, the multiplier for the arsenic content from ash to phosphorus is fixed. At high phosphate levels, this factor becomes less sensitive to Fe_2O_3 content and is at the level of 10 (meaning arsenic content in the phosphorus is 10 times higher than arsenic content in the ash).

GRAPH 1 **RELATIONSHIP BETWEEN ARSENIC IN PHOSPHORUS AND ARSENIC IN SLUDGE ASH, WORST-CASE**



In principle, this graph applies to any impurity in the sludge ash. For components other than arsenic, the result will be heavily overestimated. The sludge ash investigated in this report contains 12.7% Fe_2O_3, 21.8% P_2O_5 and 17 ppm arsenic, making the maximum expected arsenic content in the white phosphorus 12*17 = 204 ppm.

For impurities in the aluminium (scrap) that end up in the phosphorus, there is an additional factor of 0.25 (with the only assumption that the combined aluminium and magnesium content together is high (>90%)). An impurity in the aluminium of 1 ppm ending up entirely in the phosphorus then leads to a content in the phosphorus of 0.25*12*1 ppm = 3 ppm. The impurities affecting phosphorus quality depends very much on the origin of the aluminium.

With the above, it can be expected that Spodofos phosphorus may score slightly lower on arsenic compared to primary phosphorus. Organic components are not to be expected. Of the other potentially volatile components, nothing can be said in advance.

2.2.1 TESTING SPODOFOS PHOSPHORUS

From the consideration above, only chemical quality appears to be important for phosphorus applications. The sources of possible impurities are very different from those of primary phosphorus. A (first) quality determination will indicate the purity to be achieved, required process facilities in Spodofos (such as filters and staged cooling) and post-processing of the raw phosphorus.

The setup for phosphorus generation in TRL 5 is simple, so there are no facilities present to separate contaminants from the phosphorus gas stream. At this moment, it makes little sense to determine the trace elements at ppm level. Therefore, the chemical quality ‘fingerprint’ (ICP-OES) will first be determined from the raw white phosphorus. Depending on the results, further analysis may be proposed if necessary.

2.3 SLAG

Slag is the largest product stream from the process. It is roughly equal in mass to the input sludge ash.

Revenues from slag and ferrophosphorus in the basic applications [1] already lead to a financially sufficiently positive operation of Spodofos. A more useful application of the slag that also generates value could make the Spodofos concept economically attractive. With such an application, it is expected that the sustainability of the Spodofos route will also improve, and with it, accelerate the further development of Spodofos.

Recovery, regardless of revenue, is a preliminary requirement in the National Waste Management Plan, Sector Plan 22. The requirement is that no residue of phosphate recovery should be landfilled. It is important to note that due to the continuing developments of phosphate recovery technologies, this requirement may be further defined in the future.

It is therefore of great importance that the potential uses of slag are widely explored. Spodofos slag is a mineral substance, the composition of which is not yet known on any market, but which may potentially show special properties. Any added value that specific applications of the slag can provide will be examined further.

Slag from aluminothermic processes is already used in specific places. Most aluminothermic processes serve the production of valuable metals and are mostly applied in batches and on a limited scale. This is a big difference from Spodofos where slag production will be continuous and in large amounts. Furthermore, due to the varying composition of the starting materials, namely ash and aluminium scrap, the slag from Spodofos will not be strictly specified as slag from other aluminothermic processes. These aspects should be accounted for in later research.

2.3.1 FEATURES OF THE SLAG

The composition range of Spodofos slag produced from communal sewage sludge is simplified in the phase diagram below. The diagram applies to the bulk components calcium oxide (C), silicon oxide (S) and aluminium oxide (A). For simplicity, the fourth component of interest, magnesium oxide (M), has been combined with C. Content for the components Na_2O, K_2O and TiO_2 (all <2%) is assumed to negligible in this simplification.

Slag produced from the incineration ash of urban sewage sludge has a normalised bulk composition (Dutch and German average urban sludge ash from 2013, see [1]) according Table 2.

TABLE 2 **NORMALISED MEAN SLAG COMPOSITION OF URBAN SLUDGE ASH**

Component	CaO, C	MgO, M	Al_2O_3, A	SiO_2, S
Content %-mass	17±5	4±2	54±3	25±5
Content %-mole	23±7	7±2	39±5	31±5
Molar ratio	0.78±0.21		1	0.79±0.25

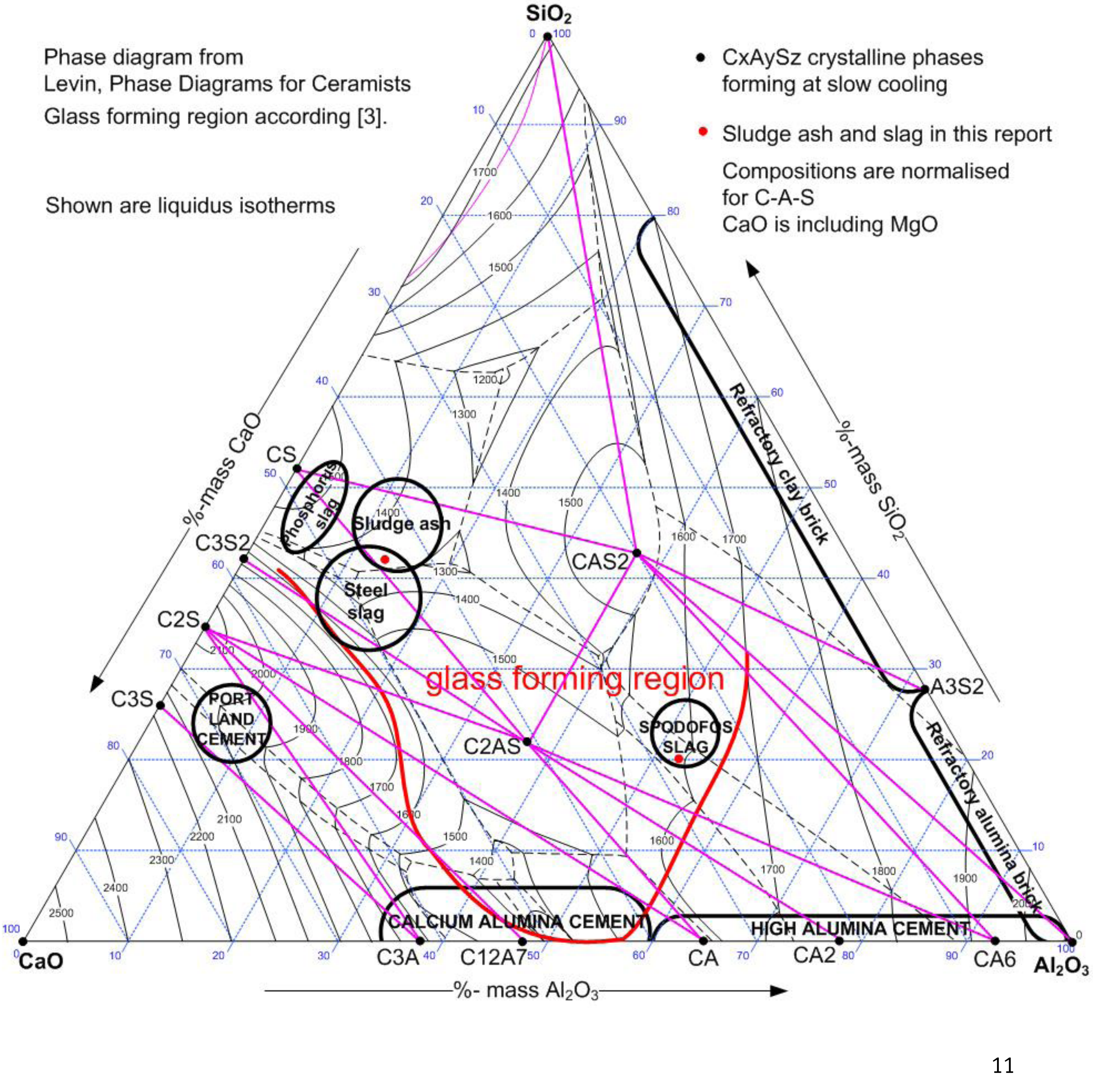
The slag is formed from a homogeneous melt. According to the glass formation region in the diagram, the slag composition is such that the liquid slag can solidify crystalline, partially crystalline and partially glassy, or completely glassy. The rate of cooling and solidification determines in which form the slag solidifies. The three most important methods:

- Slowly cooling in air (e.g. a slag bed), the slag solidifies into larger glassy pieces with crystalline phases.
- Granulating and forced air cooling (requiring a technically complex installation), the slag solidifies glassily into mostly smooth rounded pellets.
- Very quickly in/with water (e.g. a slag bath), the slag solidifies instantaneously, fully amorphous expanded slag (high porosity, so-called popcorn slag).

Very slow cooling with only crystal formation is of little technical interest but is described in literature. Crystallisation starts at about 1,600°C and ends at 1,460°C. This applies to the pure 4-component system C-M-A-S. The amounts of Na_2O, K_2O and TiO_2, are expected to lower this trajectory by about 50°C, i.e. 1,550→ 1,410°C. The lower value is the solidus of the all-crystalline material.

The direct glass former in the slag is silica (SiO_2). High alumina content (Al_2O_3) can contribute to glass formation. Alumina acts as an 'intermediate glass former'. Due to its glass nature, the softening point (glass transition temperature) of the slag will be lower than the above-mentioned solidus temperature.

FIGURE 2 **PHASE DIAGRAM CAO-AL_2O_3-SIO_2**



Phase diagram from
Levin, Phase Diagrams for Ceramists
Glass forming region according [3].

Shown are liquidus isotherms

● CxAySz crystalline phases forming at slow cooling

● Sludge ash and slag in this report

Compositions are normalised
for C-A-S
CaO is including MgO

The material in this study was prepared by either slow or very fast cooling (see figure 9). The slowly cooled slag exhibits an irregular shell-like cleavage and a matte to glossy appearance. Its colour is grey to black. Small shards are colourless. Some shards are crystal clear.

Slag solidified and expanded in water is extremely porous, mostly white in colour and is brittle with little strength.

The compact slag is identified in [1] for the base case. The expanded slag would only be desirable to produce if the slag must be ground for the application and if full amorphism is desired.

The diagram shows the composition ranges of sludge ash and Spodofos slag between those of primary and secondary mineral substances for which a market exists. This is discussed in the following paragraphs.

The Spodofos slag expressed as C-A-S in the diagram is found in an area where characteristic properties of the compact glassy material are known [4]:

Density	2.4 - 2.8 g/cm^3,
Vickers hardness	6.3 - 7.3 GPa (approx. 7 on Mohs scale; normal glass 5.5-6 Mohs),
Modulus of elasticity	83 - 103 GPa (normal glass: 70, cast iron: 100),
Fracture toughness	1.2 - 1.5 MPa/m (similar to strong concrete).

The presence of components other than C, A, and S in the slag will likely adversely affect these properties. The potentially good properties may lead to specific applications.

2.3.2 RAW MATERIAL FOR ALUMINIUM PRODUCTION

The aluminium consumed in Spodofos ends up as oxide in the slag. It is therefore a first thought to recover the aluminium from the slag, especially as the European Union has identified primary aluminium as a strategic raw material. The aluminium content in the slag is higher than that of bauxite, the regular mineral from which aluminium is extracted. The aluminium in bauxite is released via leaching with sodium hydroxide (Bayer process). Unlike bauxite, Spodofos slag is glassy and leaching with NaOH may be more laborious.

Another option is its use as feedstock in the so-called AlSiCal process [5]. Here, the alumina-containing mineral is digested with hydrochloric acid (basis is the Pedersen process). After processing, the products are pure alumina, quartz and calcite. Compared to the Bayer process, this route has a lower CO_2-footprint. Although the development of AlSiCal is progressing well, the development stage is currently in stage TRL 4.

The targeted input mineral for AlSiCal is anorthosite (consisting mainly of CAS2), of which there are large reserves in the EU. Currently, this mineral is mainly used for road foundations. If compact Spodofos slag would be used in the process, the price will not be much different from that of anorthosite. The question is whether the low price will justify transport. The expanded slag will give an advantage in processing costs as it requires less grinding energy and is easier to dissolve.

This option is to be evaluated in next development steps of Spodofos.

2.3.3 APPLICATION AS FOUNDATION MATERIAL

Provided that the environmental quality of secondary mineral substances, including residues from industry and recycled material such as crushed concrete, complies with soil quality regulations, these can find a useful application as foundation material, e.g. under roads. Depending on the quality class, there are requirements for the way the material is applied in the soil and the monitoring of the application. This is laid down in the soil quality decree.

As a quality class criterion, the chemical composition and leaching behaviour is decisive.

In addition, civil quality as a foundation material is important. Two properties of the material can be mentioned:

- compactibility: a foundation bed that can be compacted by tamping is more stable and therefore more desirable than a bed that lacks cohesion. Compactibility depends on grain shape and grain size distribution.
- slab action: some foundation materials, such as crushed concrete, shows some hydraulic action by breaking up the grains. Under the influence of water and over time, a bed of such material forms a single slab. This is very favourable for foundation applications. Slab action can also be achieved by adding cement to the base material. The latter, however, is strongly cost increasing.

Metallurgical slag is often used as foundation material. Thermphos' so-called phosphorus slag (see figure 2) generally met leaching standards. Of particular concern were the leaching of radioactivity and fluoride. The slag was applied under roads.

For Spodofos, a useful destination for the slag, where demand is constant and high, is a prerequisite for large-scale production. The application of Spodofos slag as a foundation material is therefore identified as the basic application in STOWA 2021-57. It is expected that the environmental quality is sufficient for the material to be applied without additional soil protection measures. This should be verified with tests.

2.3.4 APPLICATIONS IN THE CEMENT INDUSTRY

Mineral matter from other thermal processes often can be applied in the cement industry. In ground form, it replaces part of Portland cement, providing a significant sustainability advantage, while maintaining the quality standards required for concrete.

Substances that have a similar composition to Portland cement (OPC), such as blast furnace slag, may be suitable for this directly after grinding the slag. This substitution (up to 65%) takes advantage of the fact that the slag material has already undergone heat treatment (calcination) in the process where it was released. This greatly reduces the CO_2-footprint of the cement. Reducing the footprint is a key objective in the cement industry.

When partly replacing Portland cement with ground slag, the hydraulic action must remain intact. The hydraulic action of a cement is the ability of its constituents, under the influence of water, to develop certain mineralogical phases that give a cementing and curing action between the aggregates (sand and gravel). In this process, the wet concrete or cement mixture hardens into the form in which it is applied and develops high strength. Blast furnace slag by itself has no hydraulic action, but the cement application relies on the catalysing effect on the hydraulic properties of the slag by the Portland cement.

When partly substituting OPC with blast furnace slag, aluminium oxide in the slag is one of the limiting factors. Since Spodofos slag contains a significantly higher aluminium oxide content than blast furnace slag, this route can be ruled out for this reason alone [6]. Spodofos slag could, in the presence of hydraulic activity, supplement blast furnace slag and/or fly ash. Fly ash is becoming less available due to the decreasing number of coal-fired power plants.

Besides the most common cement and concrete, there is also calcium aluminate cement (CAC). The alumina content of this cement is between 35% and 58%. It hardens very quickly, even at placement temperatures below freezing point, and has good resistance to seawater, sulphates and heat. Due to its critical workability, it is almost exclusively used in civil works where these specific properties are important. CAC is characterised by a limited SiO_2 content (<6%) and standard EN 14647 requires alkali (Na_2O and K_2O) content 10 times lower than those expected in Spodofos slag. Slag from certain aluminothermic processes finds its way into this cement. However, Spodofos slag is again different in silica and alkali oxides.

Due to its composition, Spodofos slag occupies a place in the phase diagram (figure 2) from which cement applications are not currently known. However, due to its glassy structure, the ground slag may have (latent) hydraulic action. Should the slag be crystalline, this is less likely. The more crystalline Gehlenite C2AS and Anorthite CAS2 are both close in composition to that of Spodofos slag and show little to no hydraulic action [7,8].

The hydraulic performance of a mineral is easy to establish. Because a cement application generates value and great sustainability (without any effect on feasibility and certification processes), this test is appropriate. The results may represent a continuation or an end point for this application.

Nowadays, concrete recycling has gained a lot of attention. Urban Mine BV Zaandam focuses on recovering the separate components from end-of-life concrete. The recovered sand, gravel and remaining cement components are used to produce new concrete with minimal addition of new cement. The binder in end-of-life concrete still has about 25% of its original hydraulic capacity. This can be supplemented with primary cement. In this reprocessed cement, early strength development requires alumina content at about 10%. Spodofos slag is an attractive candidate for this, especially as its embodied CO_2 is extremely low (and will remain so in the future). A prerequisite is that an admixture of ground slag produces the desired hydraulic reactivity. This probability is highest when the slag is completely amorphous, i.e. solidified in water. Given the potential, a test with expanded, amorphous and ground Spodofos slag is appropriate.

A second application in cement/concrete is the use of slag as aggregate and filler. The main requirements are that it contains no foreign components and that the aggregate shows no alkali release, due to the highly undesirable alkali-silica reaction [7]. Since aggregate, now mostly sand and gravel, contributes less than 10% to the CO_2-footprint of the applied concrete and the coprocessing of other aggregates requires additional logistical and quality-related attention, the incentive to use secondary aggregate is limited. An important criterion when using secondary aggregates is also ‘recognisability’ at end-of-life. If secondary aggregates must be processed identically to primary aggregates at end-of-life, the traceability of the secondary material ends with potential dispersion and harmful effects on the environment.

Additionally, the low value of aggregates does not promote further investigation of this route for Spodofos slag.

Spodofos slag granules in CAC would possibly be an option when heat resistance (>500°C) is required. Then aggregates like sand and gravel are not used. Spodofos slag with the high alumina content could meet this requirement. This application is also possible in refractories, where cement types are used that are even higher in alumina (60% to 90%) than CAC. The aggregate application in refractories will be tested (see next section) with the results deciding application in CAC.

2.3.5 APPLICATIONS IN THE REFRACTORY INDUSTRY

The refractory industry supplies materials specifically for application in industrial thermal processes, for example in metal production, in petrochemicals, and in waste incineration. The task of these so-called refractory materials is to form a resistant shell for the thermal application, whereby heat losses often also must be minimised. High demands are required on these materials in terms of strength, wear resistance, chemical and physical attack, and insulation degree. Customer- or process-specific materials and structures are used, making this an industry characterised by knowledge and experience.

There are different minerals on which refractories are based. The most commonly used materials are based on aluminium oxide. As aluminium is a highly reactive metal, the oxide is very stable. The oxide has a high melting point and lifts the melting point upon mixing with other minerals. A high-alumina cement (HAC) can be composed with lime; a refractory ‘brick’ can be made with quartz (silicon oxide). In these two applications (HAC and ‘fire brick’), alumina is used to obtain a binding effect by hydraulic action (cement) and ceramic bonding (firing), respectively.

In both cases, the binding material consists of a finely ground mixture of a very specific composition. Spodofos slag will not be able to play a role in these binders because the slag composition is effectively a 1:1 mixture of these two types of binders (figure 3). Hydraulic action, as described in 2.3.3, will be measured as a characteristic of the slag and not as an intended application.

Refractory materials often consist of a binder and an aggregate. To achieve a thermally inert material, the aggregate itself and the bond between the binder and the aggregate must be thermally stable. From this perspective, it is required to apply an aggregate that is of comparable quality to the binder. Aggregates are therefore derived from specific minerals and have undergone a similar thermal treatment as the binder (1,550 to 1,600°C). As a result, unlike normal concrete/cement mixtures, the CO_2-footprint of refractory aggregates contributes significantly to the footprint of the final product. This is also why refractory aggregates are recycled as much as possible from end-of-life materials. Sustainability is a distinctive requirement of the refractory industry.

Due to its high alumina content, the application of Spodofos slag aggregate in refractory applications appears to be possible. However, Spodofos slag contains a significant quantity of calcium oxide and silicon oxide, while for the two types of existing refractories, only one of these two is present in significant amounts. The result of this deviation can only be assessed after field tests. It is desirable to carry out a first trial on both types of refractory materials.

The sustainability benefits that can be achieved with such an application are twofold: the use of secondary material and no requirement for thermal treatment. As calculated in [1] by CE Delft, if all slag is applied as refractory material, an additional CO_2-equivalent emission of about 1,000 kg/tonne of sludge ash is avoided. It is therefore a high-value application with high revenues.

2.3.6 FUSED-CAST APPLICATIONS

On the market, there are several mineral products that are produced by pouring liquid mineral into moulds in the molten state, allowing it to solidify. Post-processing may be needed. Examples include basalt tiles (Eutit.com, 1,280°C) and fused-cast refractory materials (Monofrax.com, >2,000°C), e.g. for structural elements for the glass industry. These are, from the nature of the production process, energy-intensive products, and product properties such as wear resistance and zero porosity are required in these specific applications.

The Spodofos slag leaves the reactor in molten state and can be cast directly into a mould through which a shaped building material (civil or refractory) could be produced. When processing ash from communal sewage sludge, a cost-effective scale is about 75,000 tonnes/year. The flow of slag from the reactor is then about 10 tonnes/h or 3.5 m^3/h. This amount is manageable for production of fused-cast products.

The solidification behaviour of the slag is of great importance in this process. With simple provisions, it should be possible to prevent cooling fractures or weak spots in the material. Volume behaviour is also important. In certain fused-cast refractories, a central and deep pit forms in the material at the top of the cast block. This requires intensive or undesirable post-processing. However, solidification of a glassy product gives less volume reduction than a crystalline product.

If solidification of the liquid slag and further cooling can be realised, the first step is to produce a mass product with a somewhat larger volume, e.g. stacking blocks. This is a major extension of the basic activities of the Spodofos process, but a lot of economic value is gained in such a product. The leaching behaviour of the slag is also important.

To determine the difficulty of this process, fused-casting and slag solidification will be included in the test programme.

2.3.7 SELECTED APPLICATION TESTS FOR THE SLAG

Based on the justifications mentioned, the slag will be tested for:

1. Leaching behaviour with environmental assessment,
2. Hydraulic reactivity of ground compact slag,
3. Hydraulic reactivity of ground expanded slag,
4. Application as granulate in refractory products, namely in high-alumina cement or refractory brick (basic properties are tested according to standards such as porosity and cold and hot strength, with an initial expert assessment),
5. Solidification behaviour after fused-casting (a successful casting test will include strength measurement).

2.4 FERROPHOSPHORUS

In traditional phosphorus furnaces, about 100 to 200 kg of ferrophosphorus with a content of about 25% P is produced per tonne of white phosphorus. Via this by-product, about 2.5 to 5% of the reduced phosphorus is lost.

In sewage sludge ash, the iron-to-phosphorus ratio is significantly higher than in phosphate rock and for that reason, the recovery efficiency is put under considerable pressure. Depending on the iron-phosphate ratio in the ash, in a traditional furnace, the phosphorus recovery efficiency of sludge ash can drop to 60% or less. With Spodofos, the conversion temperature will be higher, so a lower phosphorus content is expected (<15%). Even then, this has a major impact on the recovery efficiency and with it, the business case. In the pilot phase of development, a goal is to make the P content as low as possible. To this end, several methods are available.

A second approach is to post-process the ferrophosphorus, allowing a low-iron phosphate product to serve as an input to the primary Spodofos process. By volume, the ferrophosphorus is a very small stream requiring only a small plant. However, it is more desirable to achieve as low a phosphorus content as possible so that post-processing no longer adds value and can be omitted.

These options must be developed in practice. In this STOWA study, the useful application of ferrophosphorus is the subject, with or without post-processing.

When producing the ferrophosphorus for this study, the reaction conditions were not optimised. The P content in the ferrophosphorus produced as part of this study is expected to be higher than ultimately achievable in a large-scale plant.

2.4.1 PROPERTIES OF FERROPHOSPHORUS

Liquid ferrophosphorus, as it is formed in phosphorus furnaces and in Spodofos, can be thought of as a solution of phosphorus in iron. Upon solidification, it crystallises into crystals of iron phosphides with specific molar ratios of FeP, Fe_2P and Fe_3P. This results in a very brittle material.

The Spodofos material prepared in this study contains more silicon than phosphorus (see 3.5.1). The molecular ratio is $Fe_{4.6}PSi_{1.2}$. The solid material also consists of crystals made from three components: iron, phosphorus and silicon. The melting range of this alloy extends from about 1,060 to about 1,150°C [9].

Although silicon and phosphorus act similarly to the chemical resistance, hardness and brittleness of iron, the presence of silicon will affect the chemical properties of ferrophosphorus. Iron silicide is more resistant to acid attack than iron phosphide; in alkaline environments this is reversed. However, further knowledge on this subject is lacking.

The ferrophosphorus from sludge ash shows the crystal structure on the fracture surface. The material can be broken and ground quite easily with hand tools to a grain size smaller than 50µm.

Ferrophosphorus from Spodofos has a density of about 6.1 kg/dm^3 (cast form) to 6.4 kg/dm^3 (ground), this is in the range of ferrophosphorus from traditional phosphorus furnaces. On this basis, the porosity of cast ferrophosphorus is about 2%. In both forms, the material is attracted by a magnet.

Solid ferrophosphorus, which is therefore often a mixture of different iron phosphides, is a very inert material. It hardly corrodes in the air and has a lustre that it retains for a very long time. Because of its chemical stability, it can only be chemically converted under extreme conditions. The known reactions from the literature are shown in Table 3.

TABLE 3 **OPTIONS FOR CHEMICAL CONVERSION OF FERROPHOSPHORUS**

Treatment [reference]	Reaction products	Remarks
Roasting with manganese oxide MnO_2 [10]	Acid soluble Fe, P, Mn	Separation and purification necessary
Oleum [10]	Metaphosphoric acid (HPO_3)	Hydration to phosphoric acid
Heating with Chlorine gas [10]	Iron chloride + Phosphorus pentachloride (PCl_5) 670°C, in two steps	
Heating with sulphur [11]	Iron sulphide + phosphorus pentasulphide (P_2S_5)	350°C
Electric heating with $Fe_2O_3.SiO_2$ and calcined lime [12]	Iron and calcium phosphate silicate slag	1,600°C
Roasting with soda ash	Iron oxide and sodium phosphate	Refer to 2.4.4
Dissolving in mineral acid	Iron salt coagulant, phosphate	Refer to 2.4.4

The first five treatments are mentioned only to illustrate the harsh conditions required to chemically convert ferrophosphorus. Converting Spodofos ferrophosphorus with chlorine gas, sulphur, manganese oxide, oleum, or using an electric arc and iron mineral does produce a valuable phosphorus derivative, but the yield per tonne of ash is very limited and the plant to achieve this is complex and costly.

This study examines relatively simple processing and direct applications.

In any conversion, the iron product may be contaminated with trace elements (copper, chromium, lead, etc.). This can be checked in application tests.

It is expected that the copper in the sludge ash is completely concentrated in the ferrophosphorus. The Spodofos reaction thus has the effect of concentrating the copper in the ferrophosphorus by a factor of 10 to 1 to 3 mass%. This potentially provides a route to recover copper from the sludge ash as well.

2.4.2 APPLICATION IN THE STEEL INDUSTRY

The ferrophosphorus from existing phosphorus furnaces is mostly applied in the steel industry. To bring the phosphorus content in the steel product to desired value, all phosphorus in the raw liquid steel is first oxidised and the right amount is added via ferrophosphorus.

A number of restrictions apply for this application [1,18]: limited copper and silicon and no slag inclusions. For Spodofos-ferrophosphorus, copper and silicon will be present, as well as slag in negligible amounts.

2.4.3 APPLICATION IN COATINGS

It is indicated by traders of ferrophosphorus [among others: Huijin] that the material can be successfully used as a substitute for metallic zinc in coatings for corrosion protection, welding, thermal and electrical conductivity, or shielding of electromagnetic radiation. To this end, the material should be ground very fine (approx. 10 to 25 µm) and can replace a significant amount of zinc used in this process (supposedly up to 35%).

The operation in this application is probably based on maintaining electrical conductivity in the coating with less zinc. The remaining amount of zinc should still be sufficient to act in the function of sacrificial material and achieve the required corrosion resistance, etc.

In this study, a sample of the ferrophosphorus will be submitted to a coating expert for testing and evaluation. It is expected that this niche application will only serve as a very small outlet.

The sustainability of this application comes entirely from the replacement of zinc. Known zinc reserves will be sufficient for more than 100 years, so availability is on the order of that of phosphate. Since ferrophosphorus consists of only a small proportion of phosphorus, the scarcity trade-off will fall in favour of this application. Avoiding the CO_2-footprint associated with zinc production comes mainly from the electricity use in the hydrometallurgical production process. The grey energy requirement in primary zinc production is 49.9 MJ/kg (as per ISO 14025-III). The CO_2-footprint is about 3 kg/kg.

Zinc has a value of about €2,700 per tonne. The value of zinc powder is significantly higher.

2.4.4 CONVERSION TO COAGULANT AND PHOSPHATE PRODUCT

There are two relatively simple routes to convert ferrophosphorus into other products.

2.4.4.1 DISSOLVE IN MINERAL ACID

The solubility of ferrophosphorus in a non-oxidising mineral acid has not been discussed often in the literature. This is probably because the mostly available ferrophosphorus is from phosphorus furnaces (25% P). With this P content, the material is not easily soluble. At lower phosphides, however, possibilities have been found and described.

TABLE 4 LITERATURE REVIEW OF THE SOLUBILITY OF IRON PHOSPHIDES IN ACIDS

Ref	Fe_2P	Fe_3P
[13]	Most iron phosphides are insoluble or only slowly soluble in simple acids, but are broken down by aqua regia and chlorine gas	Dissolves in hydrochloric acid: $2Fe_3P + 12\ HCl + 8H_2O \rightarrow 6FeCl_2 + 2H_3PO_4 + 11H_2$ Byproduct phosphine!
[14]	Electrical, anodic solution to an iron(III) salt and phosphoric acid (a shielding $FePO_4$ layer forms)	-
[15]	-	>95% solubilisation of P in HCl, H_2SO_4 and HNO_3 (60°C)

Spodofos-ferrophosphorus contains low levels of phosphorus, but a significant amount of silicon. The question is how this works out in acid solubility.

To dissolve ferrophosphorus, it must be finely ground. Then the P content determines the degree of solubility. Several references (see Table 4) provide qualitative information on this, from which a trend can be derived:

- Fe_2P dissolves in mineral acid only under oxidative conditions,
- Fe_3P (and less P) can be dissolved in mineral acid alone.

As mentioned earlier, the presence of silicon will affect solubility.

Separating iron and phosphate into separate iron and phosphate products is a difficult task [20]. When the P content is very low, one option may be to use the solution as well as a coagulant. In Spodofos, the lowest possible P content in ferrophosphorus is pursued because it has a strong positive effect on phosphorus yield and hence the business case. In this case, post-processing by dissolution comes into the picture. Dissolution produces $FeCl_2$ and H_3PO_4 in one acidic solution, where precipitation of vivianite is not excluded. With a low Fe-P ratio, some phosphate in the coagulant could possibly be accepted.

After dissolving in hydrochloric acid, copper and possibly other components such as silicon will remain in the residue. This could be a route to recover copper from sludge ash as well.

In this study, determining how much of the ferrophosphorus as produced dissolves in hydrochloric acid was chosen as a testing strategy. A solution made through simple steps could be a starting point for further development.

2.4.4.2 SODA ASH PROCESS

The so-called Soda Ash process is a relatively simple method to recover iron and phosphorus separately. It has been extensively tested in [16] as pretreatment for the extraction of vanadium from ferrophosphorus (in P_4-production from certain phosphate ores, vanadium accumulates in the ferrophosphorus).

The ferrophosphorus should be ground to 0.15 mm, mixed with the required amount of anhydrous sodium carbonate, and roasted in a drum furnace for half an hour at 750°C. Several reactions can take place, depending on the amount of oxygen and soda. In the simplest form (for Fe_2P):

$$2\ Fe_2P + 3\ Na_2CO_3 + 5\ O_2 \rightarrow 2\ Na_3PO_4 + 2\ Fe_2O_3 + 3\ CO_2.$$

A similar reaction can be expected for Fe_3P:

$$2\ Fe_3P + 3\ Na_2CO_3 + 7\ O_2 \rightarrow 2\ Na_3PO_4 + 3\ Fe_2O_3 + 3\ CO_2.$$

At very low P concentrations, unbound iron may also be present, which oxidises immediately:

$$4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3$$

Silicon in the ferrophosphorus is also oxidised in the presence of soda [17].

$$Na_2CO_3 + Si + O_2 \rightarrow Na_2O + SiO_2 + CO_2$$

It is not clear beforehand whether the SiO_2 remains as sodium silicate or as quartz.

All metal components present, including copper, will be present as its oxide.

The sodium phosphate can then be leached with water and crystallised as hydrate ($Na_3PO_4.12H_2O$). This substance has many high-value applications.

After filtration, the iron oxide can easily be dissolved in 30% hydrochloric acid to obtain a coagulant containing trivalent iron (approx. 38% $FeCl_3$). Depending on the impurities, this can be applied in wastewater treatment.

An alternative to the crystallisation of sodium phosphate, after the iron oxide has been filtered off, is to precipitate and separate the phosphate as calcium phosphate. Then the calcium phosphate can go directly into the feed of the Spodofos process and be reduced again to white phosphorus. Since sodium phosphate is only released in limited quantity as a second P product, internal reprocessing to elemental phosphorus is probably preferred.

Calcination with soda, leaching of the phosphate product, and dissolution of the iron oxide will be tested in this study. This serves as input on the possible route choices that fit well with the primary Spodofos process.

2.4.5 APPLICATION IN DENSE MEDIUM SEPARATION

As noted earlier, the ferrophosphorus produced in this study contains a significant amount of silicon (10%). Ferrosilicon with a Si content of 14 to 16% is marketed as a density increasing agent in separation techniques (sink-float separation or dense medium separation). A suspension in water of this finely divided ferrosilicon (grain density about 6.9) can reach a density of 3.5. Such media are used in:

- the separation of ores and adherent material,
- the separation of metals from bottom ash and other sources.

It is an important technique for recycling residues or waste and reprocessing ores. For ferrosilicon, the application is based on [25, 26]:

- high density and high abrasion resistance,
- the magnetic properties (related to the recovery of ferrosilicon from purge streams from the separation process),
- its inert nature,
- the favourable price,
- easily obtaining small particles.

These properties all apply directly to the ferrophosphorus produced in this study. The total non-iron components are somewhat higher (19%), the density is slightly lower, and the price may be considerably more favourable. The CO_2 cost of ferrophosphorus from Spodofos is extremely low, which may be a major advantage.

The same and finer standardised grades of fineness of ferrosilicon for this application will be achievable with ferrophosphorus by grinding. However, ferrosilicon can also be produced in a spherical grain shape via a specific solidification technique. Mechanical grinding produces angular grains. In this application, spherical ferrosilicon grains significantly improve the rheological properties of the separation medium. This specific property of ferrosilicon, and the associated higher-value separation processes, do not seem feasible for ferrophosphorus from Spodofos. In the ‘milled application’, it may be sufficiently attractive due to a significantly lower price and low carbon footprint. Spherical ferrosilicon 15% has a market value of €1,500/tonne.

Points of interest are:

- Mobilisation of heavy metals from the ferrophosphorus to the water medium (not expected),
- The disappearance of ferrophosphorus and its impurities through the separated materials (a rule of thumb is that 100 grammes of ferrosilicon per tonne of separated product is lost),
- Possible undesirable chemical behavior in the separating medium due to phosphorus content.

A sink-float plant usually operates in conjunction with a wastewater treatment plant. This could overcome heavy metal mobilisation, if it occurs at all.

This application of ferrophosphorus cannot be quickly checked for feasibility. Expertise and multiple trials with a lot of material are required. A service provider and trading house in ferrosilicon for mining and metallurgy has been contacted for an initial assessment.

2.4.6 USE AS AGGREGATE IN HEAVY CONCRETE

For special applications, aggregates with higher densities are used in concrete. Substances include magnetite (Fe_3O_4), ‘iron shots’, ferrophosphorus, barite, etc. This achieves a strong increase in the density of the concrete, allowing for significantly smaller underwater structures or giving the concrete a high degree of nuclear radiation shielding. This saves the amount of concrete required (around 50%), as well as cement volume and associated rebar. It is also claimed that high-density concrete can be used in heat storage and vibration damping.

Of the possible aggregates in this application, ferrophosphorus and iron shots provide the highest possible concrete density. This type of concrete is referred to as high-density concrete. Concrete densities of 4,000 to 5,000 kg/m^3 are possible. The placement methods of this kind of concrete differ from normal concrete. The production of precast elements is better manageable in this respect than in situ placement.

The requirements for heavy aggregates are that they be clean, inert, free of foreign bodies and free of normal aggregates. Alkali release (alkali-silica reaction) is not an issue with these aggregates.

The application of ferrophosphorus is well known in the literature and extensively researched:

- The bond between cement and ferrophosphorus is “extraordinarily strong”, but the ferrophosphorus itself appears somewhat brittle [21].
- Sagging of the material is not a problem; processability is better than that of iron shots.
- In a broad study of concrete strength and radiation attenuation [22], ferrophosphorus comes out best on both compared to alternative aggregates.

The application of ferrophosphorus in concrete is suspected to exhibit slow hydrogen formation. The sources of this [23, 24] are not unequivocal, but similarly to all other quality effects of the application, this will require further investigation.

The price of heavy aggregates is 3 to 5 times higher than that of normal aggregates [23].

Again, end-of-life recognition of the concrete is important. In principle, separation is possible through magnetism.

Enquiries reveal that the number of projects using heavy aggregates is very limited. This application will therefore not be discussed further in this study.

2.4.7 SELECTED APPLICATION TESTS FOR THE FERROPHOSPHORUS

Practical tests for direct applications are difficult. There is relatively little material available for testing using methods such as the sink-float process.

Therefore, only expert assessment on the analysis and visual appearance of the material are done for this direct application. Practical testing will only come into play when the ferrophosphorus has its final composition (lowest in P). This will be end of pilot phase.

Testing in coatings requires the corresponding official MSDS. This has been prepared for Spodofos ferrophosphorus, and this application will be examined.

The ferrophosphorus will be further tested for solubility in hydrochloric acid. Due to the combined presence of iron and phosphate in the solution, practical applications are not expected to come into the picture in this stage. This simple test may provide useful information for further investigation.

The ferrophosphorus will also be tested for oxidation using the soda ash process. This will provide separated iron and phosphate products. The results may give further input on feasible routing of iron and phosphate.

2.5 DUST

The phosphorus gas produced in the Spodofos reactor will entrain dust and volatile components towards the phosphorus condenser. The dust is expected to consist of the smallest ash particles. This will have to be captured in an electrostatic filter and returned to the main process.

The following can be expected as volatile components: chlorides, volatile metals (such as zinc, cadmium, lead, sodium, and potassium), and arsenic.

In the pilot phase, gas cleaning will be given a lot of attention. Dust and volatiles will be largely related to the mode of operation of the reactor. The method of collecting the phosphorus in this study will be very different from that used in the pilot. At this stage, even without any gas cleaning, it is desirable to observe which volatiles are involved.

To gain insight into this, the scrubber wash water will also be analysed for components from the ash.

2.6 HEAT CONTENT OF THE SLAG

Slag is released from the reactor in molten form. Its energy content is about 2,300 MJ/tonne. At 85% of the total, this flow represents the largest heat flow from the reactor. Ferrophosphorus and phosphorus gas contribute ca. 5% and 10% of the heat, respectively.

At a processing capacity of 50,000 tonnes of ash per year, the heat in the slag stream is equivalent to 4.4 MW.

In principle, this high-grade heat flow can be regarded as a product from the reactor. However, it is extremely difficult to extract the heat from the liquid and solidifying slag. There are developments [19] to convert the heat into hot air of about 550°C. This requires complicated technology, as well as an off-taker of hot air.

The simplest way is to drain the slag from the reactor into a slag bath. From this, heat can be extracted at about 95°C. This is an appropriate level for heating purposes. However, due to the location of a Spodofos processing facility at a chempark, this energy will likely only be useable for heating buildings.

So, among other things, it depends on the location whether heat recovery is feasible or desirable. The shape of the solidified slag is also directly related to the method of cooling. At present, there are too many uncertainties and therefore heat recovery will not be investigated further.

A direct heat utilisation occurs when the slag can be applied in fused cast shaped building material (see section 2.3.6).

3

PREPARATION OF THE PRODUCTS

3.1 INTRODUCTION

Production of products requires performing the Spodofos reaction at kilogramme scales. The method of achieving representative conditions is part of TRL 5: operating the reactor. The first concern is to carry out the reaction safely. Because phosphorus gas is created, there are several safety issues: toxicity, flammability, and pressure increase. Emissions to the environment must also be prevented. The developments to create a workable and representative situation are not outlined here, only the practical implementation of the chosen method. The work takes place at GMB BioEnergie's site in Zutphen in the Netherlands.

When sufficient products have been created in batches, they are combined and processed into homogeneous products. For the individual tests, the products are post-processed if necessary (crushed, sieved, etc).

The chemical analyses of the products are included in this chapter to also derive the mass balances and distribution of heavy metals.

3.2 APPROACH

3.2.1 QUANTITIES OF PRODUCTS REQUIRED

The tests selected in chapter 2 on the products each lead to a required quantity of product. The total quantities required are calculated in the table below.

TABLE 5 **PRODUCTS TO BE CREATED**

Product	Application test	Minimum required product	Product to be prepared
White phosphorus	Analysis	2* 25 grammes	Appr. 150 gr.
		Total 50 grammes	(refer to 3.2.3)
Slag	Analysis	500 grammes	10,000 gr.
	Leaching tests	2,000 grammes	
	Refractory granulate	6,000 grammes	
	Hydraulic action	300 grammes	
	Fused casting	300 grammes	
		Total 9,100 grammes	
Ferrophosphorus	Analysis	2* 100 grammes	1,200 gr.
	Solubilization test	6* 20 grammes	
	Soda-ash leaching test	50 grammes	
		Total 370 grammes	

The proportions in which the products are released are fixed with the ash being processed: ash : phosphorus : slag : ferrophosphorus = 1.0 : 0.085 : 1.0 : 0.12. As a result, one of the products will determine the total amount of ash to be processed. The determining product is the slag. The quantity to be created is rounded to 10 kg (last column). The quantities of phosphorus and ferrophosphorus are determined in proportion to this.
As a consequence, 10 kg of ash was processed.

3.2.2 ASH, ALUMINIUM AND REACTIVE MIXTURE

ASH

Ash produced by SNB in December 2022 was chosen for this study. The composition of a homogenised quantity is shown in table 6.

TABLE 6 **BULK ASH COMPOSITION (ABOVE DETECTION LIMIT 0.02%M)**

Reacting component	**Fe_2O_3**	**P_2O_5**	**SO_3**	**CO_2**				
Content mass%	12.7	21.8	4.2	1.6				
Non-reacting component	CaO	MgO	Al_2O_3	SiO_2	Na_2O	K_2O	TiO_2	Cl
Content %-mass	22.2	3.4	7.4	22.6	0.8	1.5	0.5	0.15

ALUMINIUM

To prepare a reactive mixture, aluminium is added. Pure aluminium is used, of a specific particle size. Any other choice of aluminium (scrap) would be arbitrary. Unalloyed aluminium also contributes to the reproducibility of this study.

According to the supplier, the specifications of the liquid atomised (atomised) aluminium are:

- Assay Aluminium 99.7%,
- Particle size 63 µm.

Under the microscope, the shape of the particles appears to be irregularly elongated.

REACTIVE MIXTURE

The stoichiometric amount of aluminium can be calculated from the reacting components in the ash as shown in Table 6, which is 226 grammes of aluminium per kg of ash. As there is still limited experience and measurements of conversion in the Spodofos reaction, a slight excess of aluminium of 2% is used in this study. This compensates for not including the reduction of the more noble trace metals (e.g. CuO) and non-ideal conditions (e.g. possible aluminium losses due to oxidation to air and moisture).

The reactive mixture was prepared based on:

- 10,000 grammes of ash SNB, produced December 2022,
- 2,300 grammes of aluminium.

The mixture was intensively mixed using a concrete mixer.

REACTION

Based on the stoichiometric amount of aluminium and 15% phosphorus in ferrophosphorus and fully expiring reaction, the calculated conversion properties and products are:

- Adiabatic reaction temperature 1,820°C,
- P_4 yield: 79.5 g/kg ash (P yield 83.5%),
- Ferrophosphorus yield: 105 g/kg ash with 15% P,
- Slag yield: 1,031 g/kg ash, with expected composition according to Table 7.

TABLE 7 **CALCULATED SLAG COMPOSITION, BULK COMPONENTS**

Component	CaO	MgO	Al2O3	SiO2	Na2O	K2O
Content mass%	22.4	3.4	50.6	21.8	0.8	1.5

Based on the well-documented CaO-MgO-Al_2O_3-SiO_2 system, the solidification point (liquidus) of the slag was calculated at 1,598°C. With corrections for alkali oxides and TiO_2, the expected liquidus is 1,550°C. This temperature is important for liquid slag outflow from the reactor. For refractory applications, the beginning of the melting range (solidus) is important. However, this is considerably less documented.

The solidification point of 15% P ferrophosphorus is 1,152°C and is not decisive in process operations.
As will be shown later, the composition of the resulting ferrophosphorus differs from the calculated and expected composition.

3.3 IMPLEMENTATION OF THE REACTION

3.3.1 EQUIPMENT

The setup for TRL 5 is used for preparing the reactive mixture. Crucibles of 1 litre volume are used, with an inner lining of graphite in order to inductively heat the crucible. The outside is made from a ceramic material. This prevents the graphite from burning rapidly due to the high temperature.

The crucible is heated by an induction coil capable of 15 kW. The hollow coil is cooled by chilled recirculated water.

A cap made of heat-resistant steel is placed on the crucible. The cap is filled with refractory material so that the steel can withstand high radiation load. The cap provides connections for argon purging, temperature measurement and dosing of reactive mixture. A soft ceramic seal is put between the cap and crucible.

A second cap was used where a discharge pipe leads to a condenser, to collect the phosphorus. See 3.3.5.

3.3.2 PREREQUISITE WHITE PHOSPHORUS

An important condition for carrying out the reaction is that white phosphorus production must be limited. If more than 1 kg of white phosphorus is in storage, regulations (PGS 15) must be met. To limit phosphorus quantity, product collection is split into two methods while maintaining conditions in the reactor.

- About 3 kg of reaction mixture was processed with the phosphorus (weighing up to a maximum of 240 g excluding losses) being collected in a condenser.
- For the remaining reaction mixture, about 9 kg, the phosphorus is incinerated directly with the ambient air on exit from the reactor and the combustion gases were extracted to a water scrubber.

The ignition and complete combustion of phosphorus occurs instantaneously when the phosphorus gas comes into contact with sufficient air. This makes the execution of the reaction easier. The entire flame is vented into a suction duct. The test cabinet is also vented to a water scrubber.

In the water scrubber, the combustion product of phosphorus (P_4O_{10}) reacts to form phosphoric acid. It is known that P_4O_{10} already reacts with the water vapour in the air under formation of a phosphoric acid mist. The air from the water scrubber is emitted at a height of about 7 metres.

3.3.3 METHOD

The objective is to create representative conditions during conversion in the reactor. Representative means conditions are similar to those in a full-scale reactor. The aim is that reactions should be completed and the temperature in the reaction zone should be approximately equal to the adiabatic reaction temperature. The latter is desirable to reduce heat loss and to accurately represent the dissolution of phosphorus in iron.

At the time of processing, automatic dosing of preheated reactive mixture is not yet fully developed and therefore dosing is manual. This is a deviation from the intended full-scale situation, but this has only a minor effect on quality of representation. Another deviation is batch operation of the reactor (stopping dosing until about half-full). The reason is that in TRL 5, the continuous operation realised by continuous liquid product discharge of the reactor will not yet have been developed.

To arrive at a safe and most representative conversion, dosing tests were first carried out, incrementally in increasing amounts and with increasing phosphate content, i.e. with increasing phosphorus formation, in order not to be surprised by unforeseen hazardous situations. The enthalpy content of each ‘artificially created’ ash corresponds to that of sludge ash so that released heat and reaction temperature remain the same. Ultimately, the process described below was designed to create the products.

An amount of ca 40 grammes of reactive mixture is manually dosed to the reactor periodically and pulse-wise. The reactor is continuously inductively heated at constant temperature, approximately 1,600°C. This compensates for the heat loss that would otherwise occur between dosing pulses. The mixture is preheated at approximately 600°C so that ignition and total heat content are similar to the intended situation in a future reactor. Dosing takes place at intervals of 1 to 3 minutes.

Each batch of 40 grammes is fed into the reactor through a metal funnel, with a long and wide shaft.

Per reactor crucible, 1,600 grammes of reaction mixture is processed. If more is added, a porous slag (caused by low fluidity) will appear on the liquid slag because the slag level will be above the induction coil.

During a batch, an argon flow of 1 litre per minute is maintained on the reactor. This creates a slight overpressure that allows no or less oxygen to enter the system (allowing graphite, aluminium and/or phosphorus to oxidise).

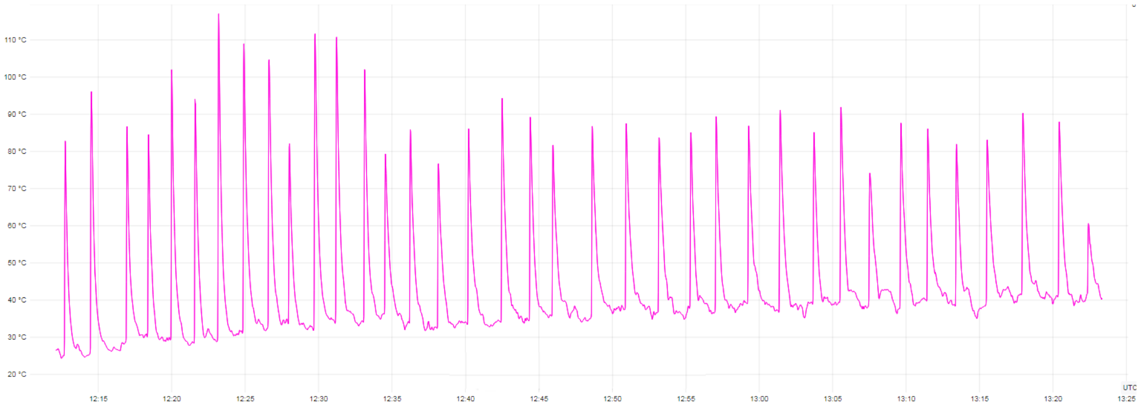
3.3.4 PROCESSING WITHOUT PHOSPHORUS CAPTURE

In order to start simple and gain routine experience, 9 kg was first processed at which the phosphorus incinerates immediately. This is possible because ignition of the mixture does not occur instantaneously but after a few seconds after dosing, when the lower layer fresh mixture in the reactor has warmed up to ignition temperature. During that time, the funnel can be removed. Through the dosing shaft, the phosphorus exits the reactor. It ignites directly on contact with ambient air. The characteristic dark yellow phosphorus flame is extracted into the water scrubber. The moment of ignition and removal of the funnel is shown in the picture.

FIGURE 3 **MOMENT OF IGNITION OF A DOSED REACTIVE MIXTURE**

A thermocouple in the ventilation duct monitors the flame as shown in the figure below.

FIGURE 4 **TEMPERATURE OF VENTED AIR DURING PROCESSING OF 1.6 KG OF REACTIVE MIXTURE**



Sometimes, dosing takes more time, which cannot be avoided. In this case, the phosphorus gas is already formed and takes (more) falling dust from the reaction mixture with it. This ends up mainly on the inside of the dosing point. Some phosphorus also condenses at that spot, creating a sticky mass. Some reaction mixture may also end up on top of the cap due to the fast handling. This is collected at the end of the batch and dosed again with the next batch.

Some irregularities can be mentioned that occur after multiple doses:

- Some phosphorus condenses at the outlet of the cap shaft. This has a sticky effect and retains dust (ash). This should be scraped away regularly between doses.
- When the funnel is not inserted deep enough into the cap, reaction mixture appears to stick at the lower side of the cap duct, reducing the passage. The cap bottom is about 1,200°C. The melting process of sludge ash is known to have started by then. The shaft is scraped clean in between.
- Occasionally, the shaft gets clogged with reaction mixture. This must be punctured and carefully scraped clean again as some phosphorus is formed simultaneously.

After all the reaction mixture of a batch has been dosed, the induction furnace is turned off and the reactor can cool down naturally. Per day, a maximum of two batches can be made.

3.3.5 PROCESSING WITH PHOSPHORUS COLLECTION

A second cap was used for phosphorus collection. This cap is fitted with a tube to the phosphorus condenser. The tube is heated with a heating ribbon to an average of 400°C.

The phosphorus condenser consists of an airtight compartment where a circulating stream of water, thermostatically controlled at 55°C, flows over a scrubber column and condenses the gases from the reactor. The non-condensable phosphorus-saturated gases, about 1 litre per minute, exit at the top of the scrubber and are extracted.

Because of the cold scrubber-end of the tube from the reactor, phosphorus tends to condensate on the wall.

After each dosing pulse, the dosing entry should be closed in order to direct the phosphorus into the condenser. This is implemented with a weight-loaded valve that falls on the dosing point after the funnel is removed. The moment immediately after dosing is shown in the picture below.

FIGURE 5 START OF REACTION WITH PHOSPHORUS CAPTURE

The overpressure through the argon purging is checked regularly to detect blockages in the phosphorus outlet. The pulse of phosphorus gas eventually gives a puff to the condenser column vent (pictured on the right).

Two batches totalling 3,000 grammes of mixture were processed in this way.

The “phosphorus pulse” from the reaction is recorded here by a temperature measurement just before condenser entry, see recording below.

FIGURE 6 **TEMPERATURE MEASUREMENTS DURING PROCESSING REACTIVE MIXTURE (1,500 G) WITH PHOSPHORUS COLLECTION**

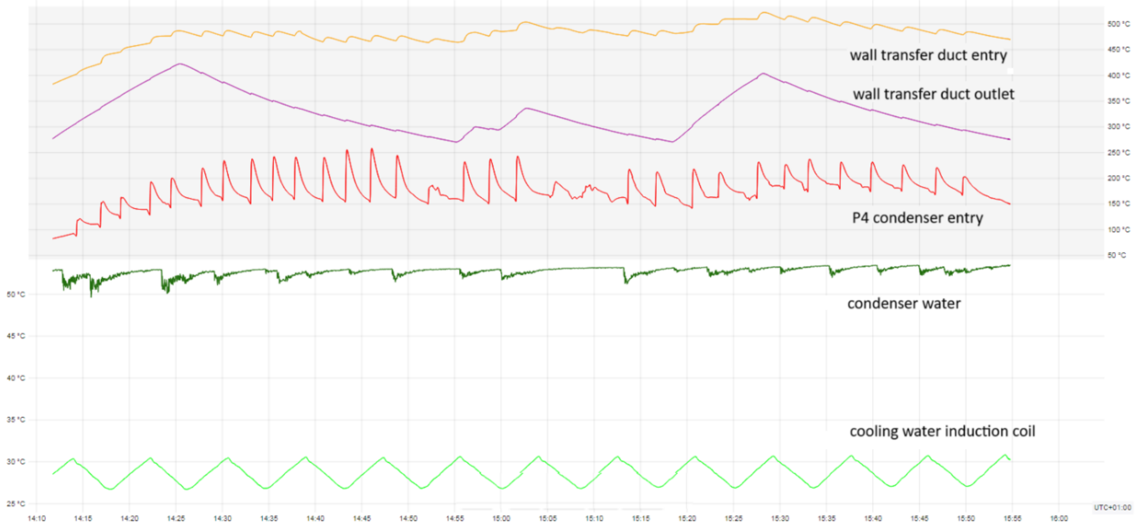
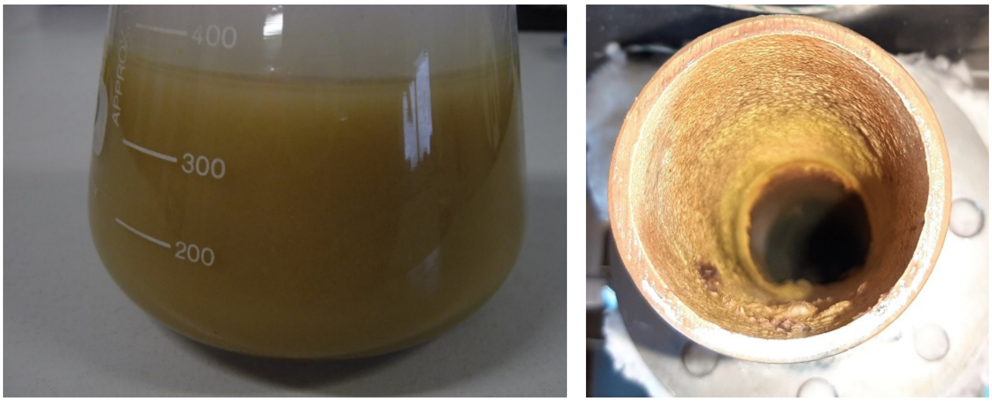


FIGURE 7 **LEFT: COLLECTED SUSPENDED PHOSPHORUS IN WATER; RIGHT: PHOSPHORUS CONDENSATION ON INSIDE COLD END TRANSFER TUBE**



Until the processing of these batches, the phosphorus condenser was not used before. An important deviation from expectations appears to occur: the phosphorus does not condense as (large) liquid droplets but in a very fine mist that is absorbed as such by the water. A suspension is formed in which the particles do not clump, and this is then circulated with the water flow. After cooling and setting, the phosphorus had to be collected from the bottom of the sump instead of the drain point under the wash column. Fine ash carried by the phosphorus gas was found in the intended phosphorus collection point. In this way, accidental separation of pure and contaminated phosphorus was achieved.

Furthermore, as anticipated, a deposit of phosphorus with ash was found at the end of the phosphorus tube between the reactor and the condenser. Thickness after two batches is about 1 to 2 mm. The tube is largely clean.

3.4 PREPARING THE INDIVIDUAL PRODUCTS

3.4.1 SLAG

After cooling down of the reactor crucible, the contents can be viewed. There are clear similarities between all batches, suggesting that the method provides reproducible results.

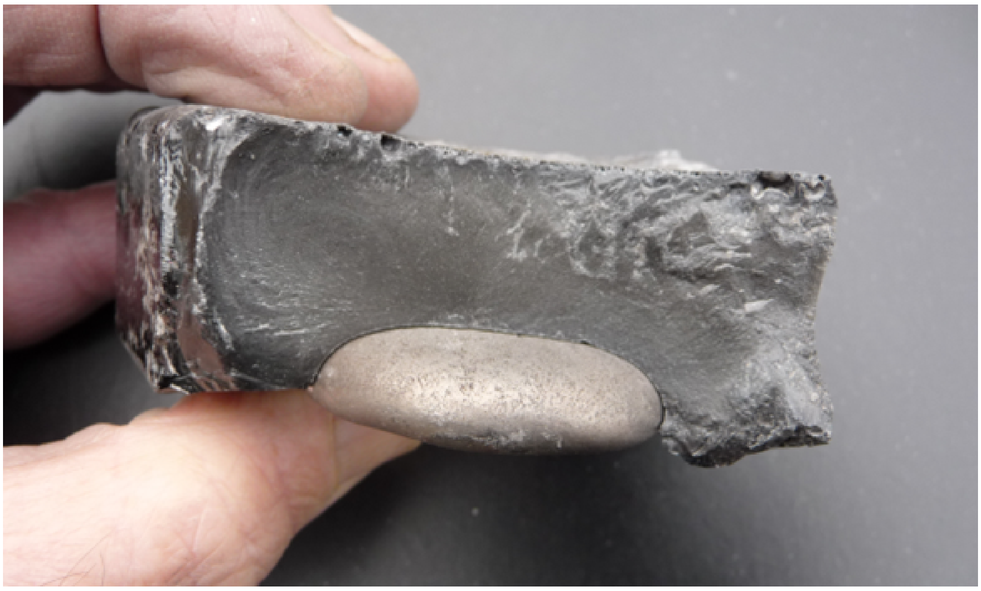
At the level of the induction coil there is a compact mass of slag (and imperceptible ferrophosphorus). Often, on top of the slag a hard slag membrane is present, which can be broken easily. The compact mass adheres to the crucible.

All eight reactor crucibles were heated again at 1,650 to 1,700°C at which the slag liquified. The batches were poured into graphite casting moulds. During rapid cooling, there is no adhesion between slag and graphite and the solidified slag can be easily collected. Graphite itself is highly resistant to thermal shock.

The membrane on the slag was found to have a significantly higher melting point than the underlying bulk. This was observed during remelting. It apparently separates due to the different crystallisation pathways of the slag: when the slag solidifies, alumina forms first. Alumina can also separate by migration to a location where the slag is below solidification temperature for a prolonged period. The membrane was broken before remelting.

The castings are cooled rapidly without insulation. Upon solidification, the mass breaks in many places. It turns out that the ferrophosphorus agglomerates very well into one large unit, at most a few drops below the slag. Slag and ferrophosphorus do not adhere to each other.

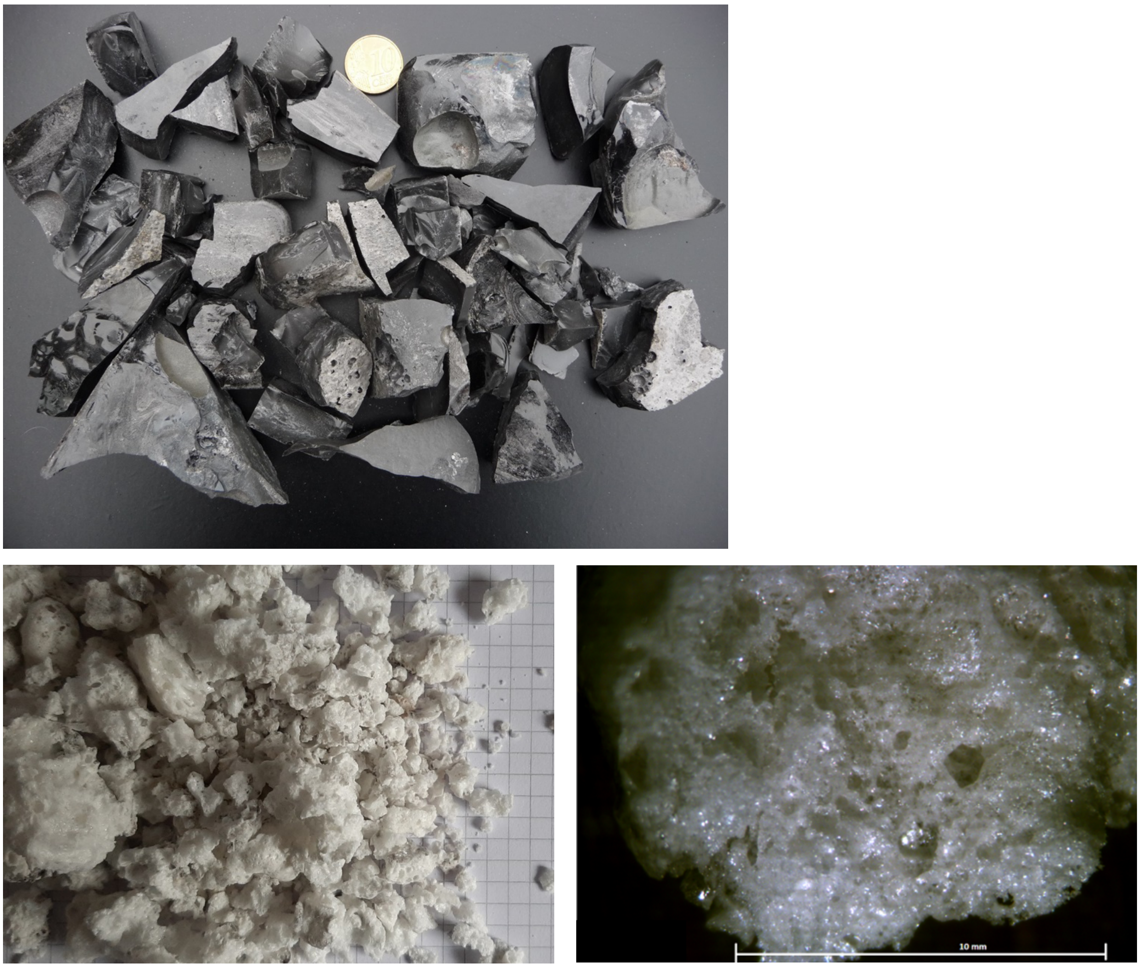
FIGURE 8 REMELTED SLAG WITH LARGE DROP OF FERROPHOSPHORUS



All slag chunks were then mixed and reduced in size by means of a jaw crusher. Different sizes were set for the different application tests. For each testing quantity, the particle size distribution was set. Because only one of the three dimensions corresponds to the set size of the jaw crusher, the other two dimensions can be significantly larger. This makes a representative particle size distribution difficult.

A small amount of slag (about 200 grammes) has been "quenched" in water (see Figure 9 below), which then takes an extremely porous appearance. Visually, this expanded slag looks homogeneous: no phases visible and completely white. Only the outer surface of the slag shows a grey to black tinge.

FIGURE 9 **TOP, CRUSHED SLAG (SLOWLY COOLED); BOTTOM: EXPANDED SLAG**



3.4.2 FERROPHOSPHORUS

The ferrophosphorus is easily collected from the moulds after cooling the slag.

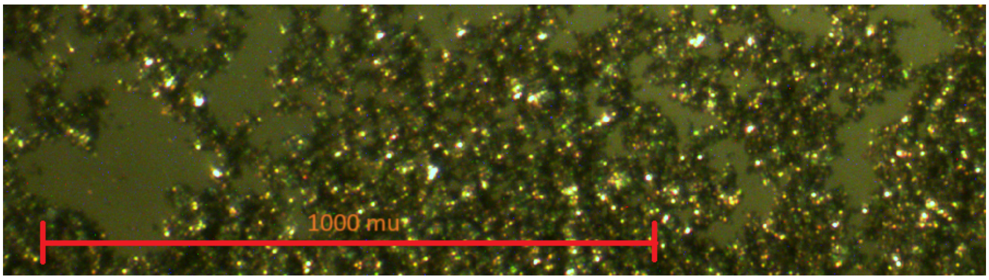
FIGURE 10 **FERROPHOSPHORUS AS COLLECTED AFTER SLAG REMELTING**

All collected ferrophosphorus (total approx. 1,000 g) was remelted again in a batch at approximately 1,200°C to form three bars (105 x 35 x 20 mm). In this process, the composition is expected to be homogeneous.

FIGURE 11 **REMELTED FERROPHOSPHORUS**

This ferrophosphorus was milled to make it suitable for heavy metals testing and analysis of various applications.

FIGURE 12 **MANUALLY MILLED FERROPHOSPHORUS, <50MM**



3.4.3 WHITE PHOSPHORUS

As mentioned earlier, the phosphorus was found as a suspension in the condenser circulation water. The clean phosphorus at the bottom of the sump was first collected under water and scooped or suctioned up. It was found that even the apparently clean phosphorus does contain some ash. It is plausible that the presence of dust favours suspension.

All phosphorus was treated in a flask with a magnetic stirrer in a water bath of up to 75°C with the aim of agglomerating the suspended and settled phosphorus particles into a pool. This method failed. It is known that a phosphorus particle equipped with a shell of (half-) oxidised phosphorus, even in an oxygen-containing environment, can persist for a very long time and thus possess a high degree of stability. A second attempt to crush the particles with a spatula (in water at 55°C) so that the phosphorus could be released also did not yield any useful results.

Distilling even the most polluted phosphorus-containing water yields almost translucently white phosphorus in the distillate. This indicates high purity. This pure form does agglomerate into a larger liquid mass.

FIGURE 13 WHITE PHOSPHORUS DISTILLED FROM PHOSPHORUS SLUDGE

The final test was to see if this white phosphorus in liquid form could be used as a ‘mixing medium’ for the thickened suspension. This was unsuccessful as well.

Consequently, the suspended phosphorus was used for the chemical analysis.

3.5 ANALYSES, MASS BALANCES AND HEAVY METALS

3.5.1 CHEMICAL ANALYSES OF PRODUCTS AND SCRUBBING WATER

ASH AND PRODUCTS

The results of the chemical analyses of ash, slag and ferrophosphorus are clustered in Table 8. The same digestion method (with hydrogen fluoride) was used for ash and slag. It was found that the contents of the main components measured via XRF are higher than the wet-chemical measured contents with ICP. The difference ‘grows’ upwards of 10 mass% for Al_2O_3 in the slag. The laboratory confirms that the XRF measurements for bulk components are safer to use for analysis. In the table below, the XRF values for the main components have been used.

TABLE 8 **SUMMARY ANALYSES REACTANTS AND PRODUCTS**

Component %-mass	Ash	Slag	Ferrophosphorus	Phosphorus suspension
Dry matter	99.9	99.9		
Component %-mass				
Al_2O_3	7.4	53.1	-	
CaO	22.2	22.4	-	
Fe_2O_3	12.7	0.0**	-	
MgO	3.4	2.4	-	
SiO_2	22.6	19.9	-	
P_2O_5	21.8	0.0**	-	
Na_2O	0.7	0.3*	-	1,700 mg Na/kg
K_2O	1.5	0.3	-	6,300 mg K/kg
TiO_2	0.5	0.2	-	
CO_2	1.6	0.0	-	
Fe	-	0.2**	76.1	
P	-	0.1**	9.2	5.7%
Si	-	-	10.4	
Mn	-	-	0.6	
Ti	-	-	1.8	
Component mg/kg				
Total S	14,300	8,530	<100	5,200
As	16.9	<1	<10	43
Cd	2.5	<0.1	<20	11
Cr	145	38.5	1,700	64
Cu	981	17.5	10,000	120
Hg	<0.1	<0.1	-	-
Pb	181	2.0	500	1,200
Ni	73.6	6.6	800	34
Zn	2,430	<10	100	10,000

*Na_2O was not measured with XRF. With TCP-ICP, Na_2O can be calculated at 0.3%

**with XRF: 0.3% Fe_2O_3 and 0.2% P_2O_5 were measured. Fe and P are most likely present as trace ferrophosphorus in the slag (see 3.5.2)

The content of elemental aluminium in the added powder is 99.7% according to specification.

SCRUBBER WATER

The scrubber water used to treat the extracted incinerated phosphorus gas was checked for volatile components.

TABLE 9 **SCRUBBER WATER ANALYSIS**

Component	Scrubber water
Quantity	82 litres
pH	4.4
Electrical conductivity	2.5 mS/cm
Orp (ref.Ag/AgCl)	275 mV
Components mg/litre	
PO_4	580
Cl	249
As	0.17
S	99
Pb	0.014
Zn	34

3.5.2 COMMENTS ON THE ANALYSES

The iron in the slag appears to be metallic iron (phosphide) because, after finely grinding the slag, about 7 g/kg of slag can still be collected with a magnet. This means that the XRF-measured Fe_2O_3 content in the slag (0.3%) is not the oxide but 0.2% metallic Fe. The phosphorus in the slag (XRF: 0.2% P_2O_5) is most likely also present as ferrophosphorus. The method of separation of slag and ferrophosphorus is easy but not yet complete (this is a point of attention in the pilot phase).

Thus, in the slag, iron oxide and phosphate are no longer present. From this, it can be concluded that the Spodofos reaction is complete.

After iron and phosphorus are reduced, a significant part of the phosphorus dissolves in the liquid iron. The ferrophosphorus formed has the molar ratio $Fe_{4.6}P$ (10.8% P) which is clearly better than the targeted Fe_3P (15.6% P). The phosphorus yield achieved was thus increased from 83.2% to 88.7%.

It appears that Na_2O and K_2O largely do not remain in the slag. The reduced amounts will most likely be evaporated given their sublimation and decomposition temperatures, respectively.

The lower concentrations of SiO_2 and TiO_2 in the slag compared to the ash must be due to the excess aluminium. Indeed, these oxides are reduced next and almost as easily after all the phosphate has been reduced.

Significant amounts of silicon and titanium were present in the ferrophosphorus. This is confirmed in the phase diagram (Figure 2), where the slag composition is below the ash-aluminium line. The expected reduction processes do not quite match the actual reduction. There are three possible causes:

- Several oxides to be reduced in the ash are present as lower oxide than expected. As a result, there is an excess of aluminium.
- The graphite wall of the reactor acts reductively on silicate (theoretically this begins at 1,625°C).
- Preferred fine sludge ash is entrained with the phosphorus from the reactor, making the remaining mixture too rich in aluminium.

The last two possibilities are due to the early stage of development. These effects may occur less frequently or not at all at later stages of development.

Copper has indeed concentrated in the ferrophosphorus by a factor of 10.

It appears from the scrubber water analysis results that the incinerated phosphorus (P_2O_5) is absorbed in only small amounts. Only about 2% of the P in the ash is recovered in the scrubber water. This corresponds to the mist seen at the emission point. Further study also shows that good absorption of P_2O_5 in water requires two venturi scrubbers as the mist is not washed out easily.

3.5.3 MASS BALANCE

When the starting materials ash and aluminium were converted, the products were not fully captured:

- The resulting phosphorus was 90% incinerated and disposed of through a scrubber.
- Fine ash particles entrained with the phosphorus gas did not participate in the reaction.
- Spatter on the upper-inner side of the reactor was not added to the slag due to possible different composition.

For this reason, product weight is not a proper basis for mass balance.

The product quantities can be calculated using the component balance of aluminium, iron and phosphorus. In each of the three products, one of these components is the most abundant. As a result, the calculation of product quantities provides the most accurate result.

Successively, the amounts of slag, ferrophosphorus and phosphorus can be calculated from the balances of aluminium, iron and phosphorus, respectively. For phosphorus, a P_4 content of 100% is assumed. However, this has not been measured.

After this simplified calculation, the total amount of products appears to be significantly lower than the reactants' weight (per kg of ash). Possible explanations for this are:

- Due to the entrainment of particularly fine ash by phosphorus gas (thereby leaving an aluminium-rich mixture behind),
- Components leave the reacting mass via the gas phase (e.g. carbon dioxide from calcite, Na_2O etc.).

To correct the mass balance, an ash loss factor is included; a fraction of the ash is considered not dosed to the reactor. For each of the four components (x = Fe, P, Al), the balance is:

$$(1\text{-}\Delta) * C_{x,ash} + 0.230 * C_{x,al} = M_{slag} * C_{x,slag} + M_{fp} * C_{x,fp} + M_{p4} * C_{x,p4},$$

Where M is the mass of products per kg of ash, Cx is the mass fraction of component x and Δ is the ash mass loss per kg of ash. M_{slag} is replaced before the solution of the system of equations by $(1.230 - \Delta) - M_{fp} - M_{p4}$.

For the compositions mentioned in the previous paragraph, the quantities follow:

- Slag: M_{slag} = 0.939 kg/kg ash
- Ferrophosphorus: M_{fp} = 0.101 kg/kg ash
- Phosphorus: M_{p4} = 0.074 kg/kg ash
- Loss: Δ = 0.116 kg/kg ash
- Total: 1.230 kg/kg ash

According to this calculation approach, a mass of up to 116 grammes of ash left the reactor prior to the reaction. This corresponds reasonably well to the 2.5% increase over expectations of Al_2O_3 content in the slag (compare Tables 7 and 8). The high silica content in the ferrophosphorus also indicates an excess of aluminium.

3.5.4 PARTITIONING OF HEAVY METALS

The calculated results for the quantities of products are retained in the heavy metal balance. Ash is retained for the quantity not recovered (Δ).

TABLE 10 HEAVY METAL PARTITIONING (ROUNDED)

Heavy metal	Fusing/boiling of the element °C	To slag	To ferrophosphorus	Gas	Theoretical* to P_4 (after cooling at 400°C)
As	613 (subl)	0%	0%	100%	10%
Cd	321 / 765	0%	25%	75%	75%
Cr	1,860 / 2,672	30%	70%	0%	0%
Cu	1,084 / 2,757	2%	98%	0%	0%
Hg	-39 / 357	-	-	-	-
Pb	328 / 1,740	1%	32%	67%	0%
Ni	1,455 / 2,730	10%	90%	0%	0%
Zn	420 / 907	0%	0%	100%	0.2%

*Based on the partial vapour pressure of the heavy metal in the phosphorus gas cooled to 400°C (90 kg/tonne ash).

Rounded percentages were calculated using:

To slag: $(M_{slag} * C_{x,slag})/((1-\Delta) * C_{x,ash})$

To ferrophosphorus: $(M_{fp} * C_{x,fp})/((1-\Delta) * C_{x,ash})$

Remainder: 100% - (to slag) — (to ferrophosphorus)

As the balances are not conclusive (in ferrophosphorus, the analyses can be considered indicative; volatile metals may condense at the suction duct's inner surface before reaching the scrubber), the partitioning was finalised partly on the basis of the expected state and the location of the associated melting, boiling, and sublimation points.

The amount that eventually ends up in the white phosphorus depends on the volatilities and the form (oxide or element) of the heavy metal. In the last column, the theoretical composition of the phosphorus gas is calculated. Up to 90% of the arsenic should condense at 400°C. This seems too optimistic. Since cadmium is present to a small extent, it does not condense below the boiling point of 400°C. Zinc is present to a large extent in the phosphorus gas but will almost completely condense. In the pilot phase, phosphorus quality in combination with specific gas treatment will have to be investigated.

Finally, it must be noted that heavy metals may be present as elements in the slag, just like iron in the slag. For ferrophosphorus, this is evident.

4

APPLICATION TESTS AND ASSESSMENTS

4.1 SLAG

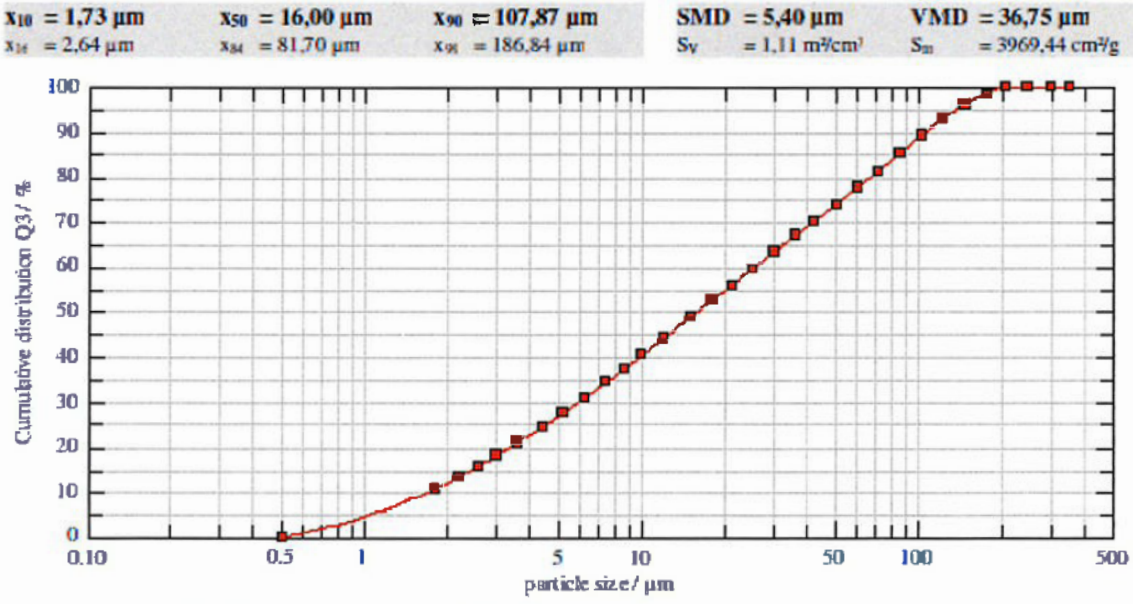
Results of the tests chosen in 2.3.7 are described in this chapter.

4.1.1 HYDRAULIC ACTIVITY

The test was carried out on slowly cooled (dense) slag by Concrefy BV in Venlo and reported under report number 2024-0297-001.

Hydraulic activity is measured by isothermal conductivity calorimetry (EN 196-11).
Before the test, the Spodofos slag was ground, and particle size distribution was measured by laser diffraction:

FIGURE 14 **GRAIN SIZE DISTRIBUTION SPODOFOS SLAG BEFORE MEASUREMENT OF HYDRAULIC ACTIVITY**



The calorimeter contains six sample positions. Three different samples were deployed in duplicate:

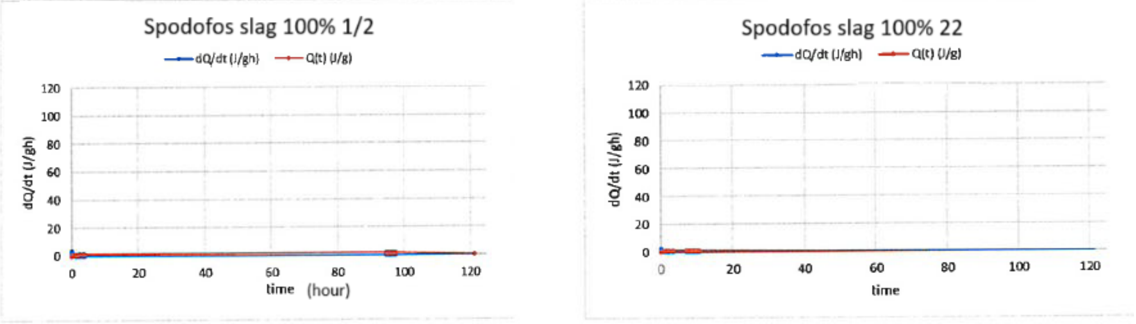
- Sample 1: 100% Spodofos slag + 0.4 parts water,
- Sample 2: 75% Spodofos slag + 25% CEM I + 0.4 parts water,
- Sample 3: 75% limestone meal + 25% CEM I + 0.4 parts water.

Sample 2 serves to catalyse any latent hydraulic activity. Sample 3 is the reference where the finely ground limestone is classified as an inert material and lacks hydraulic activity. The measurement time is 125 hours. The results are shown in the graphs below.

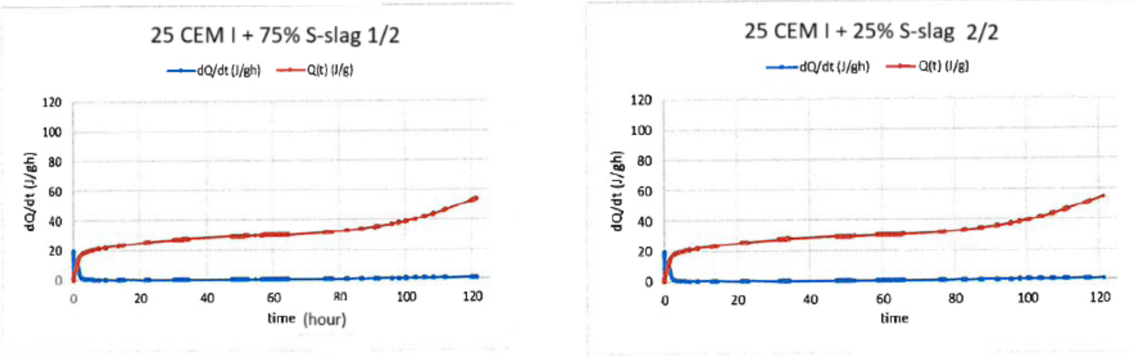
The graphs in Figure 15 show heat generation per gramme of material as a function of time. When hydraulic activity is present it is always accompanied by heat generation.

FIGURE 15 HYDRAULIC ACTIVITY MEASUREMENT RESULTS (BLUE: HEAT DEVELOPED, RED: TOTAL ENERGY DEVELOPED)

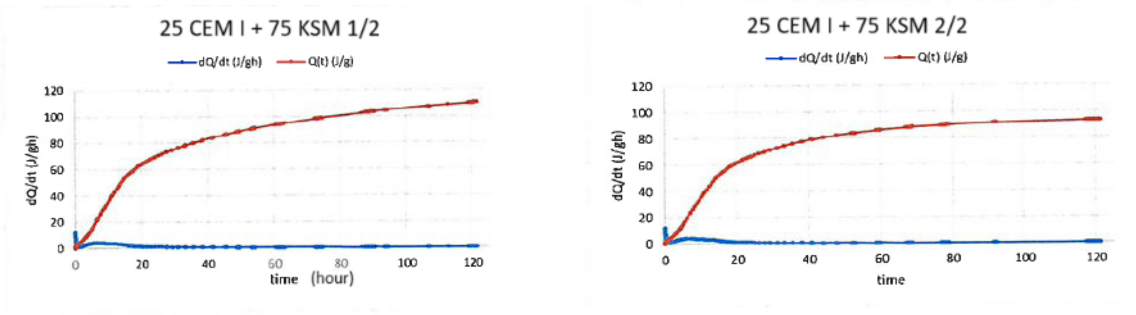
Spodofos slag 100%



75% Spodofos slag + 25% CEM I



75% Limestone meal + 25% CEM I (reference sample)



All deployed samples except 100% Spodofos slag were found to be cured after the test.

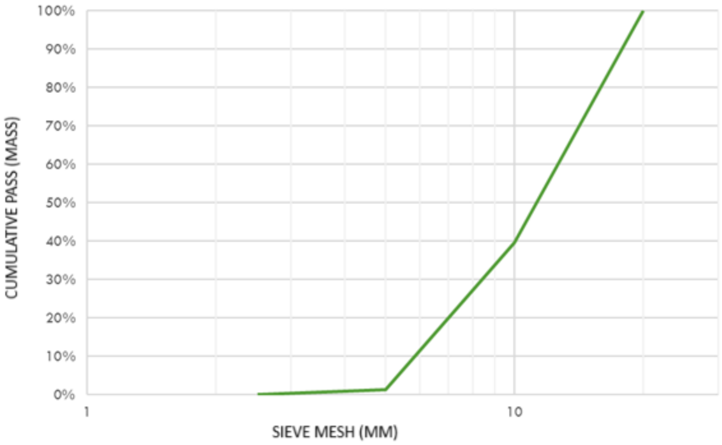
Based on the results, it can be concluded that:

- 100% compact Spodofos slag shows no hydraulic properties,
- Limestone is considered an inert material and therefore the energy released in mixing sample 3 comes only from the added cement,
- The mixed sample of Spodofos slag-cement produces a different reaction from the reference limestone-cement. It seems that Spodofos slag appears to hold back the hydration of cement, up to about 80 hours. After that, energy is still released, albeit to a limited extent.

4.1.2 CIVIL APPLICATION OF THE SLAG

For the leaching test, 1.0 kg of slag was crushed. The sieve curve of the entire batch is given in Figure 16. The finest material was not subjected to the leaching test.

FIGURE 16 **PARTICLE SIZE DISTRIBUTION OF SLAG FOR LEACHING TEST**



The leaching test was carried out by Eurofins according to NEN-EN 12457-2: for 24 hours with L/S = 10. The certificate of analysis has number 2024055001/1.
The test on emission values shows that all parameters comply with the standards (BoToVa T16). This also applies to the test against composition values (test BoToVa T17).

The overall judgment issued by Diseo BV is:
The material has been indicatively assessed as “applicable” as a non-shaped building material. The assessment took place on the basis of the standards laid down in the Soil Quality Regulations. This indicative assessment does not constitute official proof of application of the material.

CONSIDERATION OF THE TEST

As a foundation material, the compact slag granulate is a gravel substitute with no additional favourable properties: no hydraulic activity of the compact slag has been measured, and no slab formation will occur. The shape and size of the slag can, however, be controlled during crushing, possibly making a bed of slag more compactable than gravel.

4.1.3 CEMENT SUBSTITUTE

In order to lower the carbon footprint of cement, an additive with hydraulic activity is a well-known route. Fly ash or blast furnace slag are commonly used for this purpose (see Figure 2). These substances become hydraulically active when very finely ground and in contact with lime. The availability of the active components in the slag also plays a major role. Making the slag completely amorphous (non-crystalline) increases this availability.

For the tests at Urban Mine, a quantity of slag was expanded: the liquid slag is poured into water, creating a very bulky and glassy material (see Fig. 9). The composition of this slag is different from the bulk produced for the other tests. The alumina content is lower, possibly due to preferential separation in previous treatments. As a result, the other components are increased in content.

TABLE 11 **CHEMICAL COMPOSITION OF THE TESTED EXPANDED SPODOFOS SLAG**

Al_2O_3 (%-mass)	37.5
SiO_2 (%-mass)	27.5
Fe_2O_3 (%-mass)	0.6
TiO_2 (%-mass)	0.3
CaO (%-mass)	27.3
MgO (%-mass)	2.8
K_2O (%-mass)	1.3
Na_2O (%-mass)	0.0
P_2O_5 (%-mass)	1.4
SO_3 (%-mass)	2.1

It should be noted that sulphur (S) is not present in the slag as sulphate (SO_3), but in sulphide form ($S^=$). Sulphide can oxidise to sulphate and is a concern for the long-term effects of using Spodofos slag in concrete.

This material was ground to the correct fineness and tested as a substitute for Heidelberg cement. This strength determination (EN 197) is on moulded prisms with standard sand, which are made without granulate due to their small size. After certain curing times, the compression strength of a block is measured. Due to the absence of granulate, the compression strength results are approximately 80% of the strength of concrete with granulate. In addition to the mixture under investigation, a reference mixture is used.

Two formulations were made for which the compressive strength was measured after 7 and 28 days. In the recipes, the ratio of cement : substitute equals 70% : 30%.

TABLE 12 **COMPRESSIVE STRENGTHS TEST BLOCKS**

	After 7 days	After 28 days
70% Heidelberger 30% Spodofos	40.84 MPa	60.7 MPa
70% Heidelberger 30% Ecocem (reference)	43.05 MPa	67.4 MPa

Based on these results, it is almost certain that the hydraulic activity of expanded and ground Spodofos slag is sufficient to qualify it as a substitute of cement. Again, it should be noted that the slag tested was low in alumina.

Getting a secondary or new material like Spodofos slag admitted as a partial cement substitute requires an intensive development, testing and certification process. Additional questions are the long-term effects of the application, such as sulphide or alkali behaviours. As the composition of the slag also varies with the processed sludge ash, quality control on the production side of the slag is also point of attention. The test results give sufficient reason to evaluate this route when more slag becomes available. The potential sales volume in this application covers several 100 ktonnes.

4.1.4 AGGREGATES IN REFRACTORIES

Spodofos slag can be produced in two manifestations:

- Slow cooling and solidification produce a compact high-density slag.
- Rapid cooling and solidification in water produce a porous expanded slag with very low density.

Both forms have potential to be used as granulate in refractories. The expanded slag is then specific for insulating refractory products. Both applications have been investigated.

COMPACT SLAG

About 6 kg of slag was crushed and then separated into two fractions: < 10 mm and > 10 mm. These were made available to Gouda Refractories for first testing as granulate in refractory applications, as described in 2.3.5. The chemical analysis of the mixture of slag fractions was determined, the result is given in Table 12.

TABLE 13 **CHEMICAL COMPOSITION OF SLAG**

Al_2O_3 (%-mass)	53.14
SiO_2 (%-mass)	19.88
Fe_2O_3 (%-mass)	0.27
TiO_2 (%-mass)	0.17
CaO (%-mass)	22.35
MgO (%-mass)	2.37
K_2O (%-mass)	0.31
Na_2O (%-mass)	0.00
P_2O_5 (%-mass)	0.21
SO_3 (%-mass)	1.19

Based on the slag composition, it was decided to apply the slag in a normal-cement refractory concrete. This gives an indication of the applicability of the granulate in a basic concrete. This concrete is particularly applied to the inner process-specific refractory shell.

This type of concrete contains 10 to 20% cement and is made without additives (such as superplasticisers).

The expected chemical composition of the current recipe and the recipe based on the supplied slag is shown in Table 14.

TABLE 14 **CHEMICAL COMPOSITION NORMAL-CEMENT CONCRETE**

	With regular granulate	With Spodofos-slag
Al_2O_3 (%-mass)	43.23	47.29
SiO_2 (%-mass)	47.81	21.87
Fe_2O_3 (%-mass)	2.68	3.53
TiO_2 (%-mass)	1.35	0.49
CaO (%-mass)	3.62	24.15
MgO (%-mass)	0.28	2.00
K_2O (%-mass)	0.60	0.31
Na_2O (%-mass)	0.19	0.05
P_2O_5 (%-mass)	0.14	0.22

During mixing, the normal-cement concrete with Spodofos slag granulate was found to harden rather quickly, preventing the pouring of good test samples; an open structure was formed, see Figure 14.

FIGURE 17 **NORMAL-CEMENT CONCRETE, AFTER BURNING AT 1,000°C**

Based on the experience with a normal-cement concrete, the recipe has been modified towards a medium-cement concrete. This type of concrete contains 7.5 to 10% cement and contains superplasticisers. Superplasticisers are used to minimise the water content in concrete.

The adjusted chemical composition of the medium-cement concrete is given in Table 15.

TABLE 15 **CHEMICAL COMPOSITION MEDIUM-CEMENT CONCRETE**

	Phosphate concrete
Al_2O_3 (%-mass)	54.73
SiO_2 (%-mass)	23.96
Fe_2O_3 (%-mass)	0.21
TiO_2 (%-mass)	0.12
CaO (%-mass)	18.69
MgO (%-mass)	1.74
K_2O (%-mass)	0.32
Na_2O (%-mass)	0.06
P_2O_5 (%-mass)	0.16

This concrete was easy to handle and produced good samples (Figure 18).

TABLE 16 **MATERIAL PROPERTIES MEDIUM-CEMENT CONCRETE**

	with Spodofos granulate	with regular granulate (0-7 mm)
Density (g/cm^3)	2.38	2.38
Porosity (%)	17.8	18
Cold compressive strength (MPa)	34	>100

Some material properties of the medium-cement concrete were determined. These are shown in table 16.

The cold compressive strength with Spodofos slag is still very different from the optimised reference material. By also optimising the composition with Spodofos slag at a later stage, it is considered very plausible that it will comply.

FIGURE 18 **MEDIUM-CEMENT CONCRETE, FIRED AT 1,000°C, VIEWS AND CROSS SECTION**

Regular refractory granulate is usually fired chamotte clay. If Spodofos slag is successfully applied, the volume to Gouda Refractories is 250 to 1,500 tonnes. Together with other refractory producers this will be a multitude.

Because of the problems with the first test, insufficient slag was left to test for fire bricks. This test is omitted, moreover because the calcium oxide in the Spodofos granulate is unusual in fire bricks.

EXPANDED SLAG

For application as insulating granules, two properties of the expanded slag are important: maximum application temperature and granulate density. To determine these, a small quantity of slag is needed. About 200 grammes of this bulky slag was made available to Gouda Refractories for testing.

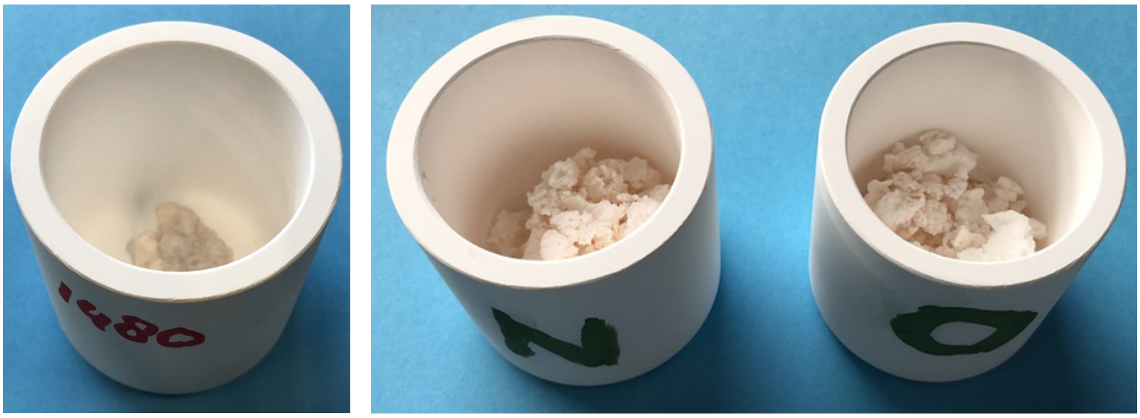
The chemical analysis of this sample was also determined. The result is shown in Table 17.

TABLE 17 **CHEMICAL COMPOSITION OF EXPANDED SLAG**

Al_2O_3 (%-mass)	50.44
SiO_2 (%-mass)	23.00
Fe_2O_3 (%-mass)	0.09
TiO_2 (%-mass)	0.23
CaO (%-mass)	21.34
MgO (%-mass)	3.15
K_2O (%-mass)	0.48
Na_2O (%-mass)	0.33
P_2O_5 (%-mass)	0.07
SO_3 (%-mass)	0.72

To determine the maximum application temperature, the material is visually assessed after exposure to a target temperature for at least 24 hours. At 1,200°C, the slag does not change at all; at 1,350°C, the slag starts to melt, and at 1,480°C, the slag is completely melted (see Figure 19). At 1,480°C, the slag does not liquify completely. If it did, due to the slow cooling, the slag would come out of the test more in crystalline opaque form. A slag with the given composition is fully liquid (liquidus at about 1,560°C).

FIGURE 19 **EXPANDED SLAG AFTER EXPOSURE TO 1,480°C (LEFT) AND 1,350°C (RIGHT, IN DUPLICATE)**



The granulate density of the expanded slag was determined to be 0.35 g/cm^3.

REVIEW OF TESTS

The compact Spodofos slag granules can lead to a different workability of the concrete mix. By adjusting the recipe, this can be remedied. However, this may reduce the number of refractory applications. The test with medium-cement concrete gave good results. The concrete properties offer sufficient perspective for developing a recipe with Spodofos slag granulate.

Proper testing requires considerably more material than was available in these first indicative tests. Due to poor workability during the first test, the test in refractory brick was omitted. When more material becomes available during the pilot phase, due to the good and valuable prospects for this application, these tests will be continued.

As an insulating granulate, expanded slag has a maximum application temperature of about 1,350°C. This makes the slag comparable to perlite, which is less common in high-quality refractory applications. If the application temperature can be raised to 1,400°C after optimisation, or when processing specific sludge ash qualities, the properties are comparable to those of lightweight chamotte. The initial results give sufficient reason to investigate this application further.

4.1.5 FUSED CASTING OF SLAG

The objective is to determine the difficulty of fused casting and obtain crack-free casting blocks.

Achieving a thin-fluid and castable slag proves easy. The softening point of the slag in the crucible can be measured with a graphite rod. When the slag no longer offers resistance to the rod, it is heated at 1,700°C for about 5 more minutes. Visually, the slag has a fluidity comparable to water. Pouring out is easy. Cast are test cubes of 5 cm.

The sensitivity of the cooling rate to fracture-free solidification was determined by treating the casting under different conditions:

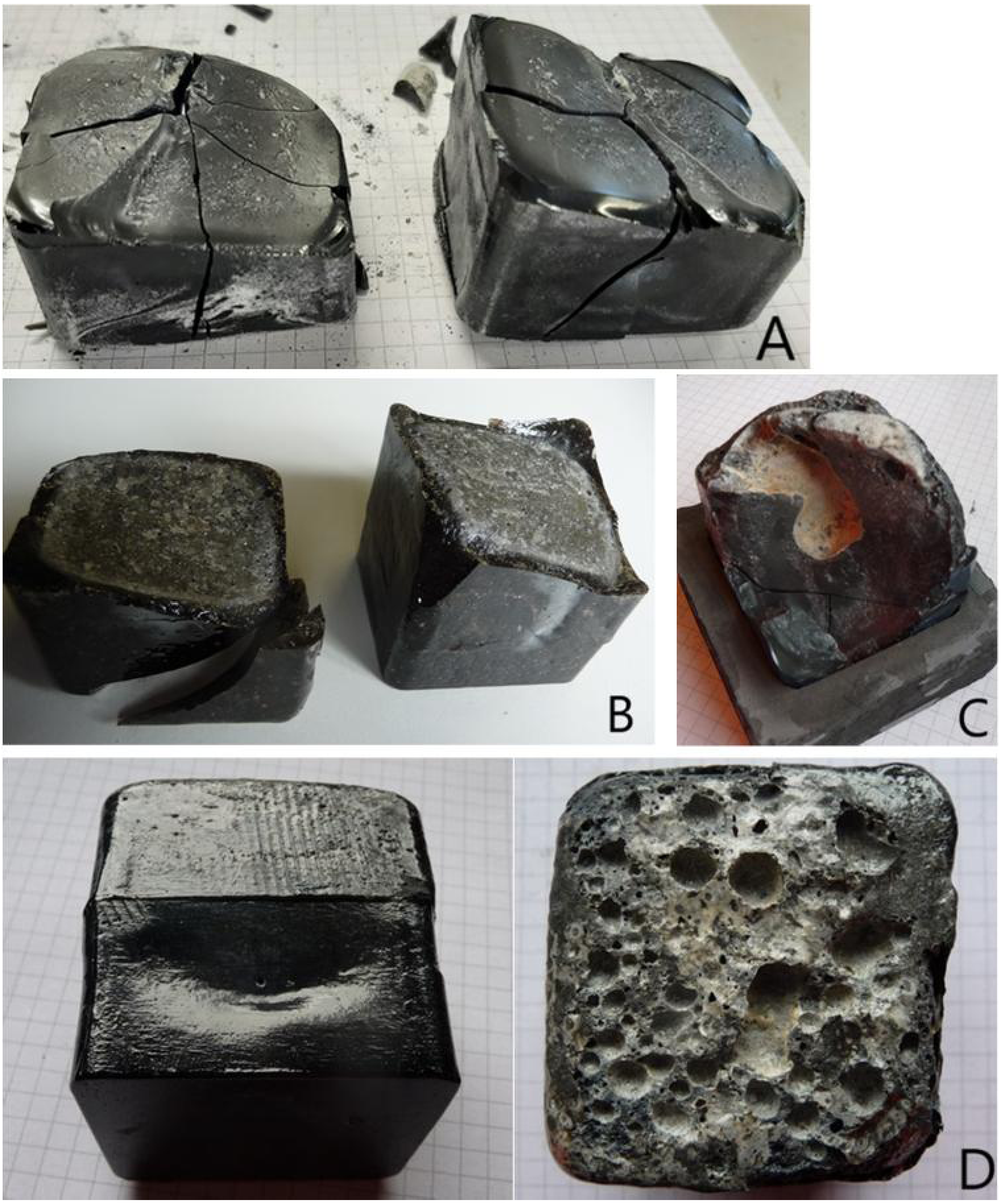
A. Cold mould, uninsulated cooling to air,
B. Cold mould, insulated cooling to air (approximately 4 cm of insulating wool all around),
C. Preheated mould 800°C, insulated cooling to air,
D. Preheated mould 800°C, cooling in oven.

After ‘demoulding’, in test A, the cube seems to be broken into many parts; in test B, two pieces are found (top edge separated); in test C, a deep hole appears in the casting and in test D, a small crack is visible along the entire top edge. The top edges detach easily.

The fracture surfaces (not in test D) show the effects of the cooling rate (Figure 20): in A the entire cube is glassy, in B is a glassy shell with a (more) crystalline core; in C the whole becomes homogeneous, not glassy.

It is thus clear that preheating of the mould and a low cooling rate are necessary to prevent solidification stresses and cracking. In addition, test D shows bubbles below the surface, covered by a thin shell of slag. The height is also somewhat reduced compared to immediately after casting. Furthermore, the cube is glassy and smooth at the perimeter and bottom of the casting mould, except for a slight contraction (dent 3 mm) at three side faces. It is therefore also necessary to cast slightly (0.5 -1 cm) higher and remove the excess material later. However, the casting then becomes too high for the kiln used.

FIGURE 20 **MELT-CAST SLAG CUBES AFTER DIFFERENT COOLING METHODS ACCORDING TO LIST A-D**



The strength of cast slag can be measured on the result of test D. The standard dimensions of a specimen in a compression strength test is a 50 mm cube. This differs here with H x W x D = 48x47x50 mm.

FIGURE 21 FUSED CAST TEST BLOCK AFTER FAILURE IN COMPRESSION TEST

The compression test was carried out by Gouda Refractories. The cube was loaded on its side because of the irregular shaped top side. A cardboard has been placed on the two compression surfaces so that the uneven surface is evenly compressed. The (indicative) strength is 100 MPa (inset: scale in kN, dividing by 2.5 is MPa). This is comparable to the strongest concrete class.

Although during the pressure test the crack sounds indicate inhomogeneities, the fragments after failure do look homogeneous. Another remainder of ferrophosphorus (D = 4 mm) was found between the shards.

CONSIDERATION OF THE TEST

When fused casting slag into shaped (building) materials, the heat content of the liquid slag is also utilised. It turned out that cooling or solidification of the slag is critical but attainable through simple means. The contraction on solidification is limited and the top of the cast piece is irregular. The strength of the material is high. This application has such a high degree of difficulty that the initial experience should only be seen as input for any subsequent developments.

4.2 FERROPHOSPHORUS

The tests described here were selected in 2.4.7.

4.2.1 PHOSPHORUS SOURCE FOR STEELMAKING

To assess the application of Spodofos ferrophosphorus in the steel industry, Tata Steel's Process Management Department was contacted for advice and information.

Of the prepared ferrophosphorus, the content of two components (P and Si) are well outside the Tata Steel specifications for the currently applied ferrophosphorus. A lower phosphorus content should, in principle, not pose an issue, and silicon could be brought to or below required levels during the Spodofos process. Manganese and titanium content meet the specifications. No customer restrictions apply for residual components (possibly As, Cd).

There are no specifications for copper. Copper is kept at very low content in the steel product. The copper content of 1% in Spodofos-ferrophosphorus can still be accommodated by a lower dosage of P to the steelmaking process. When copper becomes a critical issue, it could still be compensated with a higher P content in the ferrophosphorus.

The main objective of the Spodofos process is to optimise operational costs and product yields. The obvious method is to make the P content in ferrophosphorus as low as possible in order to increase the P_4 yield, while finding useful applications for the remaining iron alloy. This makes the ratio of critical components to phosphorus in the iron alloy more unfavourable for application in the steel industry.

The current purchase price of ferrophosphorus by Tata Steel can be translated to about €2.30/kg P. The significantly higher value of white phosphorus and the potential value of the remaining iron alloy in other applications confirm that large-scale marketing phosphorus to the steel industry is unlikely. This needs to be verified at a later stage of development.

4.2.2 ZINC SUBSTITUTE IN CORROSION PROTECTION COATINGS

For this assessment, the assistance of a coating expert from a Dutch paint manufacturer was necessary, and tests were executed under supervision.

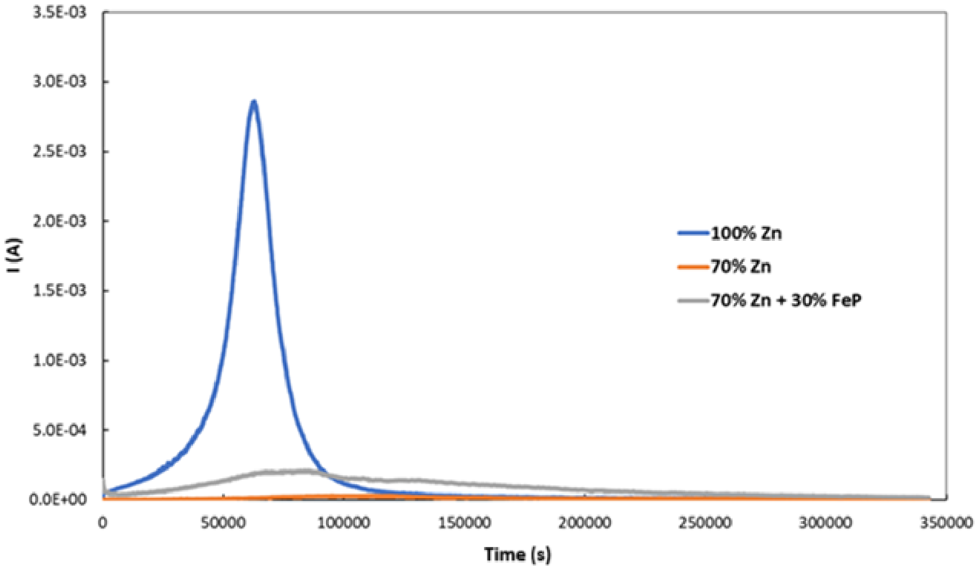
Prior to testing, it was assessed that the ferrophosphorus was a potentially interesting replacement as a partial zinc substitute. A lead content in the entire coating of <100 ppm was set as a limit. This seems realistic.

The ferrophosphorus was incorporated into a commercial Zinc primer. The following samples were tested:

- Zinc primer as standard recipe (100%-vol Zn),
- Zinc primer with reduced zinc (70%-vol),
- Zinc primer with ferrophosphorus (70%-vol zinc and 30%-vol ferrophosphorus).

First, the electrochemical response of the different systems was measured. Figure 22 shows the current that can be generated through the zinc primer as a function of time. Integrating this graph, we see that about 14.4% of the zinc oxidises for the purpose of cathodic protection.

FIGURE 22 **CURRENT THROUGH COATING**



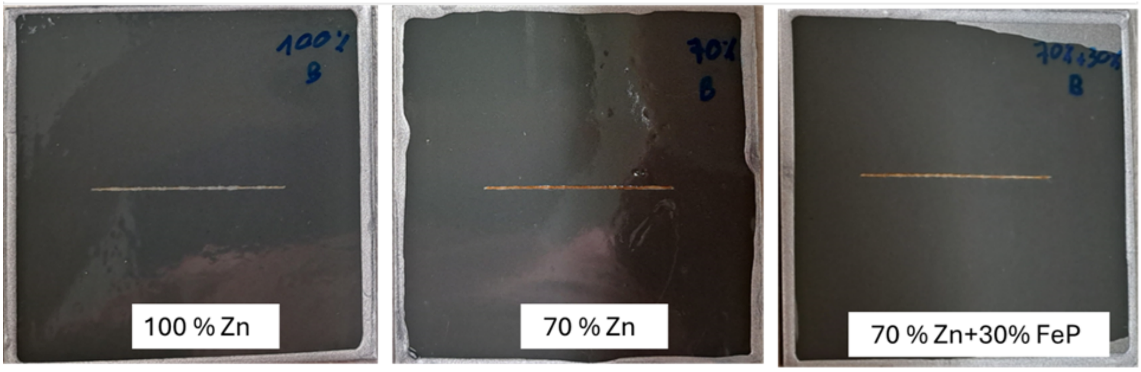
In the test coupon where the volume of zinc is reduced to 70%, connectivity is lost and the electrochemical response changes. This reduction allows only 1.2% of the zinc to oxidise (normalised to 100% volume).

Adding 30% volume of ferrophosphorus should improve connectivity. Indeed, the electrochemical response shows increased current, and 6.3% of the zinc oxidised.

Although there is some substitutional effect, the current for cathodic protection of the sample with ferrophosphorus is significantly lower than the reference sample.

The coatings were then subjected to an accelerated corrosion test (Prohesion, ASTM G85 annex A5 - dilute electrolytic cyclic fog/drying test) for 72 hours. After this time, the first red rust already appeared in the scratches of the coatings, containing 70% zinc and 70% zinc + 30% ferrophosphorus. This indicates that the electrochemical response of these coatings is not sufficient to protect the substrate.

FIGURE 23 **VISUAL ASSESSMENT CORROSION TEST**



A slight positive effect can be seen, however, as the sample with ferrophosphorus shows less red corrosion product than the 70% zinc sample.

In conclusion, ferrophosphorus has a small positive impact but cannot be considered a direct replacement for zinc. It seems that considerable reformulation efforts are needed to confirm ferrophosphorus as a zinc substitute. Tests show that its conductive properties are not sufficient.

These results, combined with experience with other zinc reduction technologies, will not lead to further testing with this material.

4.2.3 SUBSTITUTE FOR FERROSILICON IN DENSE MEDIUM SEPARATION

The assessment of the feasibility of using Spodofos ferrophosphorus as a dense medium agent in sink-float processes instead of ferrosilicon (15%), see 2.4.5, was requested from a consultant in this field, who is an international commodity trader in metallurgy and mining. The DMS process is used worldwide in the separation of light metals and ores from mixed streams. These separation processes have huge throughput volumes, so fluctuations in yield represent large financial losses or gains.

For this reason, such processes are fine-tuned, and highly specialised/very specific materials are used. The specifications of ground ferrosilicon (15%) from the producer cover properties that enable the sink-float application, in particular grain size distribution, 14 to16% Si and density, but also the chemical composition (C, P, and S content). However, the composition has no direct impact on the process and could therefore vary among applications.

The application of Spodofos ferrophosphorus as a 100% substitute for ferrosilicon is initially seen as a decent possibility, perhaps even a desirable one, for two available grades. There are four conditions:
- The separation process must not lose efficiency; this requires a pilot programme.
- The ferrophosphorus should meet specifications (which are not yet known).
- No appreciable leaching must occur of ferrophosphorus in water (see below).
- The net financial effect of changes in separation efficiency and alloy loss must be at least comparable to regular ferrosilicon.

A lower price compared to current used products and an extremely low carbon footprint will support the Spodofos ferrophosphorus in this application.

The global trading volume of ferrosilicon (15%) for DMS is estimated at 50,000 tonnes. It is concluded that Spodofos ferrophosphorus certainly has opportunities to fulfil part of this.

In this study, ferrophosphorus is available with 9.2% P and 10.4% Si. In further development of Spodofos, a lower P content in the alloy will be targeted (5% or less). However, the silicon content in ferrophosphorus can be modified while maintaining the required properties of the material. Therefore, for this application, trials are only appropriate when the overall process is further optimised, i.e. during the pilot phase.

LEACHING IN WATER

For application in dense medium separation, leaching of heavy metals into water may be a concern. This was measured after long-term (14 weeks) contact of the ferrophosphorus (<50 µm) in water at room temperature, with an L/S ratio of 10.

TABLE 18 **LEACHING OF FERROPHOSPHORUS IN WATER**

SGS ICP analysis, report SR-6320974.01.A01 (July 2024)	Eluate (ferrophosphorus – water)
pH	7.65
Fe	<1 mg/kg
P	1 mg/kg
Pb	<1 mg/kg
Zn	<1 mg/kg

These figures indicate that leaching is unlikely to be a concern for the application of Spodofos ferrophosphorus in dense medium separation.

CONSIDERATION OF THE REVIEW

The material properties and inert behaviour of Spodofos ferrophosphorus led to a positive expert assessment. The material should be extensively tested in larger quantities for application in dense medium separation.

If application testing is successful, utilisation of all produced ferrophosphorus is almost assured. The value of the replaced ferrosilicon material is high. Additionally, the application takes place in processes that generate sustainability (such as metal and plastic recycling and ore beneficiation).

4.2.4 CONVERSION TO COAGULANT

4.2.4.1 SOLUBILITY IN HYDROCHLORIC ACID

The ferrophosphorus produced contains a low phosphorus content, which makes it soluble in hydrochloric acid. However, it also contains an equal amount of silicon. Like phosphorus, this has a stabilising effect on the iron. The solubility of the ferrophosphorus was determined under the following conditions:

- Ferrophosphorus ground to <100 µm,
- hydrochloric acid 30%,
- amount of hydrochloric acid (mol) equal to double the amount of iron (mol) plus a 10% excess,
- 60°C (water bath), until end of hydrogen production.

25 grammes of ferrophosphorus were used. Per gramme of ferrophosphorus, 3.7 grammes of hydrochloric acid 30% was added.

After treatment, the solution was filtered. The residue was rinsed with water and dried. The filtrate and the acid-free residue were analysed.

Measured gas production totalled 3504 Nml (after 20 hours at 60°C). This is assumed to be hydrogen. Corrected for barometric pressure, temperature, water vapour pressure and the water column in the measuring cylinder and this volume corresponds to 156 mmol of hydrogen gas. After completion of the reaction, the suspension was filtered under vacuum.

TABLE 19 **QUANTITIES MEASURED**

	Prior to reaction	After reaction
Dry matter	25.0 grammes of ferrophosphorus	23.9 grammes of filter residue
Liquid	92.5 grammes of HCl 30%	91.5 grammes of filtrate
Gas	-	0.3 grammes of hydrogen (calculated)
Total	117.5 grammes	115.7 grammes

With some loss of liquid, the resulting measurements are reasonably balanced.

The filter residue is still magnetic.

TABLE 20 **ANALYSES OF THE FILTRATE AND RESIDUE**

	Solution (ferrophosphorus – 30% HCl) SGS report SR-6320974.01.A01	Ferrophosphorus residue MME Group report 2746/1
Fe	23,100 mg/kg	75.1%
P	930 mg/kg	5.3%
Si	N/a	15.1%
Pb	1 mg/kg	<0.1%
Zn	3 mg/kg	<0.1%
Cu	72 mg/kg	1.3%
Cr / Ni / Mn / Ti	N/a	0.2% / 0.1% / 0.8% / 1.5%

The metal residue has the formula $Fe_{7.9}PSi_{3.2}$.

In the liquid, the molar ratio equals Fe : P = 14 : 1.

Of the heavy metals in ferrophosphorus, less than 3% Cu, 1% Pb and 10% Zn were dissolved.

TABLE 21 **POSSIBLE CONTROL BALANCES**

Balance	Assumption	Result
Iron		Starting mass 19.0 grammes ←→ in residue + in sol. 17.9 + 2.2 = 20.1 gr
Silicon	Si does not dissolve	Starting mass 2.6 grammes ←→ 3.6 grammes in residue
Phosphorus		Starting mass 2.3 grammes ←→ in residue + in sol. 1.3 + 0.09 = 1.4 grammes
Hydrogen evolution	1 mol H_2/mol Fe 2.5 mol H_2/mol P	45 mmol H_2 calculated←→ 156 mmol H_2 measured

Except for iron, the balances are far from conclusive. It seems that all remelted ferrophosphorus was not homogeneous in terms of composition.

CONSIDERATION OF THE TEST

The alloying elements P and Si exhibit a strong nonreactive effect on iron. The presence of both elements in the ferrophosphorus lead to low solubility in 30% hydrochloric acid. Less than 10% of the ferrophosphorus is dissolved. Due to the inert matrix, only 10% of zinc also dissolves. Dissolution is an oxidation reaction of iron and phosphorus, but the assumed reaction equation is not supported by the measured gas evolution. As a result, the reaction is not (yet) understood. The element balances are certainly not conclusive with this first test.

The test confirms the suspicion that this method of converting ferrophosphorus to a coagulant is ineffective. Despite having a higher Fe/P mole ratio in the liquid relative to the ferrophosphorus, it can be said that the processing route has low efficiency and is still misunderstood. The only result that can be attributed to this processing is that the residue is nonreactive to an even greater extent.

4.2.4.2 SODA-ASH LEACHING

For the roasting of the ferrophosphorus (76.1% Fe, 9.2% P, 10.4% Si, other components excluded), the literature assumes reaction equations appropriate for experiments. Based on the available information, the applicable reaction is:

$$Fe_{4.6}PSi_{1.2} + 2.7\ Na_2CO_3 + 5.9\ O_2 \rightarrow Na_3PO_4 + 2.3\ Fe_2O_3 + 1.2\ Na_2O + 1.2\ SiO_2 + 2.7\ CO_2$$

The soda is consumed by the base forming components such as P and Si; the metals are oxidised by atmospheric oxygen. Per gramme of ferrophosphorus (96% $Fe_{4.6}PSi_{1.2}$), 0.85 grammes of anhydrous soda is required. Since the above reaction equation is on the safe side as far as soda consumption is concerned, no excess is maintained here.

The entire process consists of four parts, three of which have been implemented:

- Roasting with anhydrous soda,
- Leaching of the water-soluble salts, followed by filtration and washing of the residue,
- Crystallisation of the eluate,
- Dissolving filter residue in hydrochloric acid.

Crystallisation was not performed because the solution probably contains several crystallising components in larger amounts (e.g. sodium silicate, residual soda) so the composition is not yet the desired one. The extract was analysed for the bulk components.

ROASTING

Ferrophosphorus roasting was carried out under the following conditions:

- Ferrophosphorus ground to <100 µm, quantity 30 grammes,
- Soda ash 25.5 grammes, ground in ferrophosphorus powder,
- Heated to 750 to 775°C for 3 hours; air overblow 2 l/min, and contents stirred every 15 minutes.

After starting the roasting, a reaction can be clearly seen as a (quiet) flame emerges from the mixture. The mass sintered into a lump, and this was crushed in a mortar after one hour of roasting, see Figure 24. With further roasting, the mass remained granular.

FIGURE 24 **FERROPHOSPHORUS ROASTING; CONTENTS AFTER 1 HOUR**

The amount of roasted product is measured after treatment.

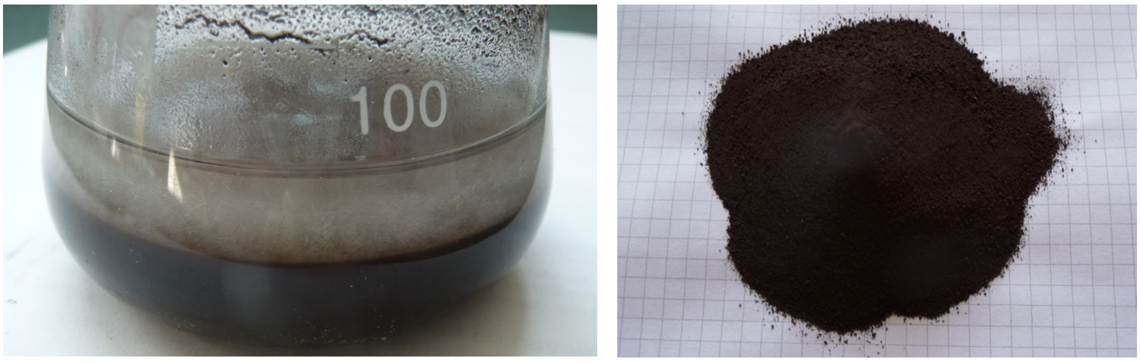
Before and after the reaction, total mass in the crucible was measured to be 55.45 g and 59.64 g, an increase of 7.5%. The weight increase according to the expected reaction is 6.5 grammes (+11.7%). This difference may be partly explained by the fact that iron was not converted into Fe_2O_3 (red in colour), but into Fe_3O_4 and FeO, and iron silicates.

The material clearly underwent a reaction: it consists of black-grey-brown clumped powder.

LEACHING AND FILTRATION

The entire reaction inventory mixture was shaken with 100 ml water at 90°C for 15 min. After cooling, a layer of crystals formed on the iron residue. The crystal dissolved in its own crystal water between 30 and 35°C possibly indicating $Na_2CO_3.10H_2O$. After supplementing with another 100 ml of water, no more crystal formation occurred upon cooling. The pH of the extract was 11.0.

FIGURE 25 **PHOSPHATE EXTRACT AND IRON OXIDE RESIDUE**



The suspension was then filtered after which the residue was rinsed with a total of 1.5 litres of water. This water was light brown turbid.

The composition of the phosphate extract and residue is shown in Table 22.

DISSOLVING THE RESIDUE

After air-drying the residue, it appeared granular brown-black under the microscope. There were no more particles with metallic sheen, at most a few reflective spots. It was easily ground, and it was attracted to a magnet. Because of the colour, it can be assumed that the iron is not present as Fe_2O_3 (red), but as Fe_3O_4 and/or FeO.

38.4 g of air-dried residue was collected (with some iron loss in the rinse water). After drying at 105°C, the moisture content was determined to be 3%. The residue was then heated at 400°C for 1 hour to decompose any hydrates present. The mass reduction amounted to only 1.4%. The final ‘harvest’ was 36.7 g, see Fig. 25.

In order to get as much material in solution as possible, a large excess of hydrochloric acid 30% was used.

The filter residue of 36.7 grammes contained 22.8 grammes of iron (derived from 30 grammes of ferrophosphorus 76.1% Fe). Used for dissolution are:

- 30 g anhydrous filter residue,
- 200 g hydrochloric acid 30%.

It turns out that the residue only partially dissolves in the hydrochloric acid: a dark brown liquid is formed above a voluminous sediment. Even after prolonged heating to 60°C, the sediment layer remains.

The sediment was rinsed several times and decanted, filtered and dried. The yield is 11.81 grammes. Corrected for the total ferrophosphorus deployed, this is 11.81 * 36.7/30.0 = 14.4 grammes.

TABLE 22 COMPOSITIONS

SGS report SR-6320974.01.A01	Phosphate extract 230 gramme	Residue dissolved (in 30% HCl) 260 gramme (calculated for 36.7 gramme residue)	Non- or slightly soluble residue 14.4 gramme XRF
Fe	6 mg/kg	63,000 mg/kg	65.3% Fe_2O_3
P	17,300 mg/kg	135 mg/kg	4.7% P_2O_5
Pb	<1 mg/kg	3 mg/kg	<0.1%
Zn	<1 mg/kg	8 mg/kg	<0.1%
Cu	ND	860 mg/kg	0.3% CuO
Si	530 mg/kg	ND	23.1% SiO_2
Na	47,100 mg/kg	ND	<0.1%
CO2 (own analysis)	6,200 mg/kg	-	-
Ti	-	-	5.9% TiO_2
Cr + Ni + Mn oxides	-	-	0.8%

ND: not determined

Metal balances (Fe, Cu, Ti) are well balanced here. 72% of the iron is dissolved. The powder is still magnetically sensitive.

CONSIDERATION OF THE TEST

This first soda-leach test provides a lot of information.

The sodium balance on leaching is correct. The phosphorus balance is not conclusive. Double the amount of P is measured in the extract than present before the reaction, but it can be said that all phosphorus goes into solution. The extract contains very little iron. Lead, zinc and probably copper dissolve little or not at all. Remarkably, silicon becomes only slightly mobile, only up to 3% of the Si in ferrophosphorus.

The recalculated mole ratios in the extract are Na : PO_4 : CO_3= 2.0 : 0.6: 0.14 with which the composition of the extract at pH 11.0 can be said to be Na_3PO_4 and Na_2CO_3 in the mole ratio of about 4:1. It can also be stated that the added anhydrous soda was in limited excess. According to the carbonate balance, 86% was found to have reacted.

Of the iron oxide residue remaining after leaching, dissolving it in concentrated hydrochloric acid proved extremely problematic. This seems to be related to the conversions during roasting. The silicon has not become mobile and remains in the residue. Under the microscope, the air-dried residue looks extremely amorphous and ‘cemented’, with white, light brown and grey or black phases. At some spots, silver or golden reflections can be seen. A reference was found that this oxidation method can lead to a quartz layer on the other material, shielding it from the acid.

To investigate this in more detail, the residue was analysed using LIBS (Laser-Induced Breakdown Spectroscopy), SGS report SR-6326145.01.A01, with the eye (microscope) at different phases (white, light brown and grey or black) being analysed separately. See Figure 26 for the results.

There can be no ‘phases’ after this analysis. Silicon is present everywhere as silicate and quartz and is coloured by other elements in low concentrations. In specific spots, titanium(oxide) is seen. This leads to the conclusion that the virtually insoluble residue consists of iron silicates and possibly -titanates, further embedded in and cemented by quartz. Calculated volumes of iron oxide and quartz and titanium oxide are approximately equal in the composition found. Therefore, with all the information, it is plausible that the iron is immobilised and/or shielded from the action of acid by silica and titanium oxide.

FECL$_3$ PRODUCED

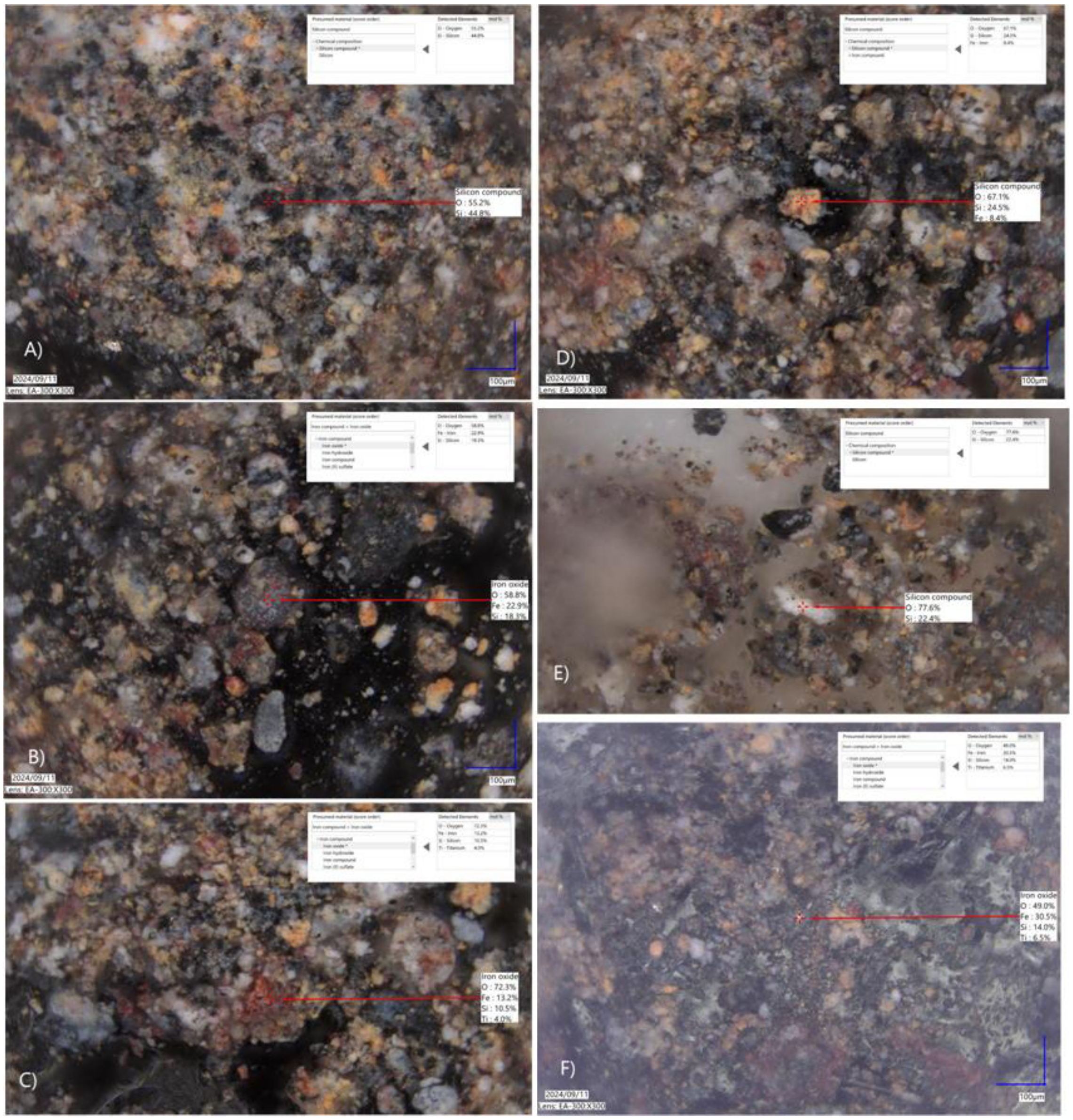
It is expected that all iron oxide in the leached residue dissolves in concentrated hydrochloric acid. However, this was measured to a limited extent. The ferric chloride solution contains 72% of the Fe originally present. The remaining iron oxide and almost all the silicon are in the insoluble residue. Zinc dissolves 70%, lead 5%, copper dissolves 75%.

SUMMARY

The release of phosphorus from ferrophosphorus proceeds as expected with the soda-ash leaching method. It is an effective method to separate iron and phosphorus in ferrophosphorus. The phosphorus product (sodium phosphate) can possibly be converted into calcium phosphate, which in turn can be fed into Spodofos. The P yield (to white phosphorus) can become very high in this way. However, if subsequently the iron residue must be dissolved in hydrochloric acid, the negative effect of silicon in ferrophosphorus becomes noticeable: a significant part of the iron is not dissolved because it is rendered partially immobile by a shielding layer of quartz and silicates.

With the added amount of hydrochloric acid, a ferric chloride was obtained with 6.3% Fe. Commercial ferric chloride contains 40% $FeCl_3$, or 13.8% Fe. When no or significantly less silicon is present in the ferrophosphorus, the desired concentration of ferric chloride can be achieved. The impurities that can be expected are residual P-PO_4, Pb, Zn and especially Cu at the 0.3% level.

FIGURE 26 LOCAL COMPOSITIONS OF INSOLUBLE RESIDUE; RESPECTIVELY.AN A) BLACK, B) BROWN, C) BROWN/RED, D) WHITE, E) LIGHT BROWN AND F) REFLECTING PARTICLE (COMPOSITIONS IN MOL%)



5

EVALUATION OF RESULTS

5.1 WHITE PHOSPHORUS

White phosphorus is the main product and does not require application testing. However, the required quality may be an issue. In the TRL 5 test set up, no provision has yet been made to clean the phosphorus gas from dust and volatile components from the ash before condensation. As a result, the phosphorus produced was captured in a very impure form. High-quality white phosphorus was extracted from it by distillation. The high quality is characterised by an almost colourless appearance.

If dust and volatile components are adequately captured, as envisaged in the following stages of development, it should be possible to directly extract good quality white phosphorus after filtration. The quality will be determined by arsenic in the sludge ash. This parameter will be similar to conventional high arsenic white phosphorus. Other quality parameters of conventional white phosphorus are expected not to be an issue in the Spodofos process.

5.2 SLAG

The tests and expert assessments carried out, confirm the special application potential of Spodofos slag. The basic application of the slag in the feasibility study [1], as foundation granulate under roads, has been superseded due to positive results and the large market potential of the slag in refractories or as a partial cement substitute.

From the test results and the very positive reviews and expectations of experts, expanded slag has the best prospects. Expanded slag is formed during rapid cooling, making it completely amorphous and highly voluminous. This material can be used with high probability as a partial cement substitute, and it has good potential as insulation granulate in the refractory industry.

The sales volume to cement is so large that in terms of sludge ash, a multiple of Dutch ash production can be sold. The low CO_2-footprint of the materials is the driver for the processing industries to use such materials in their products. Compared to sludge ash, slag is also greatly reduced in heavy metals: only chromium remains to a small extent. In the aforementioned applications, chromium oxide does not qualify as a pollutant because of its immobility and its natural presence in primary materials.

The other route is the slower cooling of the slag resulting in a glassy and hard material. This form was taken as a baseline in the previous study [1], with the applications being foundation material and granulate for refractories.

In the application as foundation granulate, the environmental quality complies to the regulations but there are no additional positive properties: it only replaces gravel and shows no slab effect. However, this application is always possible.

In its application as a refractory granulate, test results exceed expectations. The slag would replace material that has to be mined and fired at a high temperature, achieving a great sustainability gain. This applies to both slowly solidified compact slag and rapidly solidified expanded slag. Since expanded slag can be used in cement in large volumes, production in this form is the most straightforward choice. If the slag in compact form can acquire a market position in the refractory industry, it would be a focus for the next stages of development, in order to determine how the slag can be partially produced in the compact form. Aggregate application in CAC can also be investigated at a later stage (see 2.3.4).

Experiments have been carried out on fused casting the slag, to gain insight in the feasibility and difficulty of this processing. In principle, the production of pre-shaped building materials or refractory elements is possible, and the formed material is very strong. However, a lot of additional processing would be required. Later stages of the Spodofos development will determine whether to follow up on this option.

5.3 FERROPHOSPHORUS

In the preparation of the test material, due to the unoptimized process, ferrophosphorus was obtained with a lower phosphorus and a somewhat higher silicon content than expected. The physical properties of this material were all found to meet the required properties of ‘dense medium agents’, the substance suspended in water for density-based separation and refining of metals and ores. The assessments of ground ferrophosphorus by a service provider and raw material supplier in this regard were very positive. Also considering the high value of the regular material, a sufficiently large and global market is expected for this application. As for impurities, the ferroalloy contains lead, copper and nickel. However, the alloy is inert, and these materials do not leach to a noticeable extent.

This application still requires a lot of test material and intensive field testing.

To achieve raw material reuse from the wastewater chain, the conversion of ferrophosphorus to coagulant (ferric chloride for use in water treatment) is a highly desirable objective. There is a route to achieve this, whereby also the phosphorus in the ferrophosphorus eventually becomes an additional yield of white phosphorus.

A test for this so-called soda-ash leaching process was carried out in this study. The conversion of iron and phosphorus to iron oxides and a phosphate is straightforward. The phosphate, after leaching and precipitation, can be returned to the feed of the Spodofos process and converted into additional white phosphorus. Due to a higher silicon content in the ferrophosphorus in this study, problems arose in dissolving the iron oxides in concentrated hydrochloric acid. A significant proportion of the iron oxides does not dissolve because silicon oxides or silicates render the iron immobile.

With this knowledge, it is possible with a high degree of certainty, to develop process operations that will produce the desired results. However, this comes at the expense of the simplicity of the Spodofos process. It involves several post-processing steps and a considerable purchase and processing of chemicals. The main uncertainty is the presence of copper in particular, within the ferric chloride coagulant (0.33% Cu). How to deal with this (permitting, removal, recovery) is beyond the scope of this study.

Tables 34 and 35 show the mass balance for this ‘$FeCl_3$ route’.

In the application of ferrophosphorus in anti-corrosion coatings, part of zinc is replaced. The test results indicate that with the intended replacement of 30% zinc by an equal volume of ferrophosphorus, the corrosion properties are not sufficiently maintained. The paint manufacturer therefore chose not to pursue this application further.

The ‘standard application’ of ferrophosphorus in the steel industry is not possible with Spodofos ferrophosphorus, due to low P and high Cu and Si content.

5.4 HEAVY METALS

In this study, the partitioning of heavy metals in the sludge ash to the three product streams is very clear and reasonably in line with expectations (see also Table 10):

- Only some of the chromium remains in the slag; other heavy metals are greatly reduced.
- Copper, nickel and residual chromium accumulate in the ferrophosphorus. About 1/3 of both lead and cadmium end up in this product.
- The remaining heavy metals (arsenic, zinc, cadmium, and residual lead) become volatile in the reactor and are carried away by the phosphorus gas stream.

If the phosphorus gas stream is adequately stripped of the entrained heavy metals before condensation (arsenic will be removed to a small extent), significantly cleaner products are left than the output sludge ash:

- The slag is extremely low in heavy metals, meeting leaching standards.
- The ferrophosphorus is an extremely inert (stable) alloy; leaching has not been observed.
- The phosphorus will contain almost only arsenic, at levels not unusual for commercial phosphorus.

Together with the valuable uses of these products, end-of-waste status should be achievable for each.

The capture of heavy metals from the phosphorus gas stream will produce a lead and zinc-rich byproduct. The basis of this will be sodium and potassium. This stream will amount to ca. 3% of the sludge ash (30 kg/tonne). If, in a later stage of development, this stream is collected, further investigation can determine an appropriate application.

6

NEW BASIC DESIGN AND BUSINESS CASE

6.1 BASIC DESIGN

In STOWA 2021-57 [1], the basic design of the Spodofos plant was configured on the basis of the calculated product ranges and expectations for market opportunities.

With the results of this study and the market volumes and prices that can be estimated with greater certainty for Spodofos products, the Spodofos plant can be further improved in design.

In particular, this concerns slag and ferrophosphorus applications. These are significantly better than tentatively assumed before [1]. In addition, it can be expected that the heavy metals in the products will no longer play an effective role, so that ‘end-of-waste’ status may possibly be in sight to convert the waste sludge ash into (unique) products.

With high probability, slag can be fully utilised as a cement substitute. The market volume for this exceeds several hundred thousand tonnes per year. Since fly ash is becoming increasingly less available and the CO_2-footprint of Spodofos slag is very low, problems in marketing can reasonably be excluded. Its value can be tentatively set at the value of fly ash, with the advantage of sustainability for the customer. The success rate for this application is rated high by a key market player (Urban Mine).

For the first Spodofos plants, the ferrophosphorus can be fully used as a substitute for ferrosilicon (15%) used in separation techniques. Its applicability, due to its similar properties and lower price, is rated highly by an international market player.

Further research is needed for both applications. The two market players are enthusiastic and hopeful about the likelihood of success. On the Spodofos development side, the focus is on controlling the quality of the two materials within not yet specified margins.

In the table below, the differences in product applications compared to the previous draft are juxtaposed.

TABLE 23 **CHANGES TO THE BASIC DESIGN AS A RESULT OF THIS STUDY**

	Base design STOWA 2021-57	Updated design
Slag	Gravel substitute for foundation applications; value €10. Partial application: refractory granulate; value €130.	Cement substitute; value €40.
Ferrophosphorus	No application and value assigned (€0)	Substitute for ferrosilicon in dense medium separation; value €500.

These two products allow the Spodofos plant to remain simple and compact. Only limited post-processing of the products is required before they can be sold. The partial application as insulating granulate in refractories is not included here. Thus, revenues are reserved.

The phosphorus produced continues to have the same outlet to the chemical industry.

The heavy metals will have to be separated from the phosphorus stream with some dust and alkali metals. There may be opportunities for zinc recovery, but at this stage, the application of the dust remains limited to landfill.

During the past development phase, the choice of aluminium source also became clear: there is sufficient aluminium available, recovered from the metal fraction of bottom ash from municipal waste incineration. Although this has yet to be demonstrated, this aluminium is expected to be more efficient for Spodofos processing than in aluminium smelting.

6.2 BUSINESS CASE

Based on the modified design, the business case can be better prognosed. The specifications described below are calculated based on a processing capacity of 50 kt of ash per year.

The same ash composition as was used in STOWA 2021-57 is assumed as the weighted average of SNB and HVC of certain years. The bulk composition is described in Table 24.

TABLE 24 **STANDARD COMPOSITION SLUDGE ASH FOR BUSINESS CASE**

	P_2O_5	Fe_2O_3	SO_3	Al_2O_3	CaO	MgO	SiO_2	Remainder
%-mass	22.9	13.9	2.8	6.8	16.4	4.2	21.9	11.1

Differences from the business case in report STOWA 2021-57 are:

- Now, the aluminium to be used is from bottom ash from domestic waste incineration (previously higher quality secondary aluminium). The aluminium content has been adjusted to 88% (previously 100%).
- The preheating of ash and aluminium is now set worst-case at 700°C (previously 600°C).
- After drying with waste heat, the final heating of aluminium is inductive (previously natural gas),
- Through optimisation and an excess of aluminium, it is expected (based on the tests carried out) that ferrophosphorus grades up to 5% P and high silicon content can be produced (previously 15% P).
- This increases phosphorus recovery efficiency by almost 10% to 94.1%.
- In connection with the production of expanded slag, not a slag bed is projected but a slag bath. This also allows the heat in the slag to be reused at about 95°C.
- The dust residue to be landfilled is found to contain a significant proportion of alkali metals from the ash and is increased from 10 to 30 kg/tonne of ash.

The inputs and outputs of this envisaged situation are, per tonne of fly ash:

• Aluminium	269 kg (€1,000/tonne, 88% Al)
• Phosphorus	94 kg (€3,650/tonne)
• Slag	1026 kg (€40/tonne)
• Ferrophosphorus	119 kg (€500/tonne)
• Dust (mostly alkalis), to be landfilled	30 kg (€300/tonne)

The gate fee of fly ash here is kept the same as in 2021 at €90.

The annual amounts of energy and auxiliary materials required for process operations are:
- Natural gas: 1,200,000 m^3 (left equal due to higher temperature of just the ash),
- Electricity: 6.8 GWh (more than double due to inductive aluminium heating),
- Diesel oil: 70,000 litres,
- Chemicals: 75 tonnes.

The updated business case is an extrapolation of the 2021 business case. No new (budget) quotations have been requested for the investment costs of the new configuration, but a factor compared to 2021 is used, as well as for the costs of consumables.
- Energy and chemical costs are 180% higher.
- For the investment cost, 130% of the 2021 investment is used and increased by the cost of inductive aluminium heating (budget statement manufacturer 2023) and an estimate for the slag bath and ferrophosphorus post-treatment.

Based on the above mass balance, material prices, process modifications, investment and operating costs, the simple payback time and return on investment for a plant with a capacity of 50kt of fly ash (approx. €26M capex) is described in Table 25.

TABLE 25 **INDICATORS BUSINESS CASE, FIRST DESIGN (2021) AND UPDATED DESIGN (MID-2024 PRICE LEVEL)**

	Base design STOWA 2021-57	Updated design (this study)
Payback period (years)	5.1	3.1
Internal Rate of Return (10 years)	13%	30%

The business case becomes significantly more favourable because of the high-value product applications. Although not yet calculated in detail, the extremely low payback period shows that sensitivity to scale and investment size plays a minor role. The strong business case can be entirely attributed to the unique and high-end applications of the phosphorus, slag and ferrophosphorus products and the compact process operation.

6.2.1 STABILITY OF THE BUSINESS CASE

In Spodofos operation, purchased aluminium is by far the highest cost, approximately €270 per tonne of sludge ash (as determined as price level in mid-2024). In contrast, the revenue from phosphorus is higher, approximately €345 per tonne of sludge ash processed. The sensitivity of the business case is therefore greatest for both these commodities. This requires explanation because both markets are not widely known.

Three aspects can be identified that affect both prices.

AVAILABILITY AND SUSTAINABILITY

The market volume of secondary aluminium in Europe is approximately 6.0 Mt, of which 1 Mt is exported to the India region [27]. If all Dutch sludge ash (by 2027, three sludge mono-combustors, approximately 85,000 tonne) were to be processed via Spodofos, the aluminium procurement would be approximately 20 kt or 0.3% of the European market. Spodofos will therefore not distort the aluminium market, and the price will continue to be determined by smelters.

Secondary white phosphorus is not yet available on the market, but it is an important item for the phosphorus processing industry to reach set sustainability goals. Dependence on few existing producers also plays a role. The phosphorus from Spodofos has a significantly lower

CO_2-footprint than primary white phosphorus as an extra (see chapter 7). This is certainly also a market advantage. By using the regular price of phosphorus in the business case, problem-free sales can be assumed. The quality of phosphorus is still an issue (see section 3.4.3).

ELECTRICITY

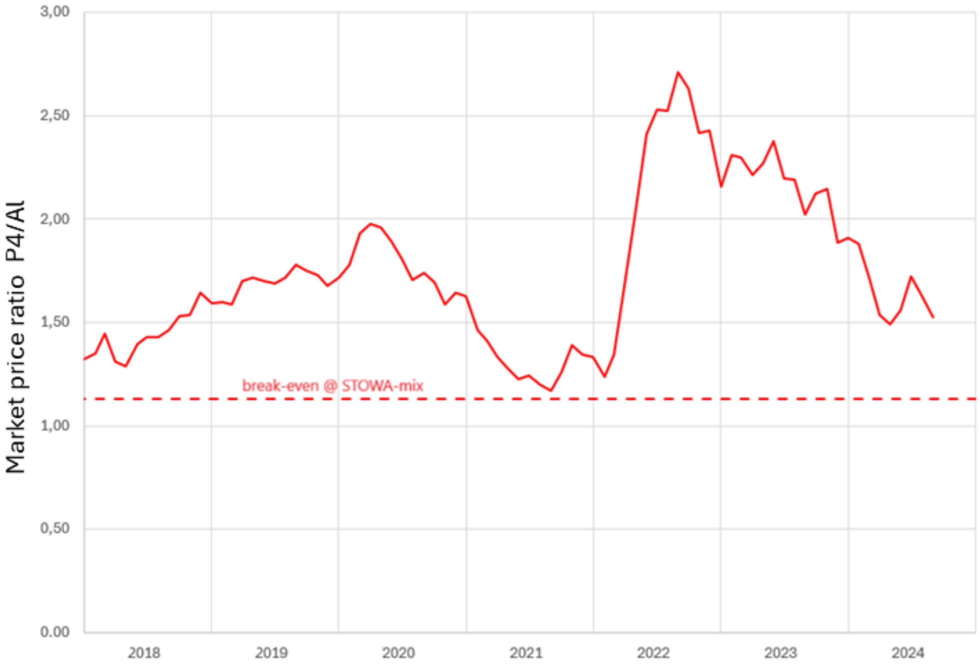
Both aluminium and white phosphorus are raw materials where electricity costs at production determine the market price. Energy inputs are high and comparable for both. Both prices will therefore move with the energy price.

ECONOMIC STABILITY

Due to global incidents between 2020 and 2022, commodity prices have become highly volatile in 2022 [28]. After an initial large and rapid increase, prices have slowly stabilised at an intermediate level. The effect of commodity price movements on the Spodofos business case can be represented by the ratio of phosphorus price to aluminium price. This is calculated for the last six years, as seen in Figure 27. Shown is the price of white phosphorus, relative to the price of primary aluminium on the London Metal Exchange (LME).

The prices of the different grades of secondary aluminium follow the LME price as a percentage thereof. With the amount of aluminium required for the Stowa mix sludge ash (from domestic waste incineration), the percentage of the LME used, and the amount of phosphorus produced, the phosphorus revenues become equal to the aluminium costs (break-even) at a ratio of 113%. The historical level of the P_4/Al ratio is around 120%.

FIGURE 27 WHITE PHOSPHORUS TO PRIMARY ALUMINIUM (LME) PRICE RATIO AROUND RAW MATERIAL SCARCITY IN 2022



The payback period at the lowest point this period (2021), at the 2021 investment and raw material price level, is 4.0 years and the internal rate of return (10 years) is 21%.

The quantity of raw materials required for phosphate ore and bauxite per tonne of finished product and their share in the price of the finished product is similar. However, the bauxite price is considerably more stable (up to an increase of 30% over the past 10 years) than the price of phosphate rock (peak movement of up to 300%). With this, it can be expected as shown by the 2022 graph that this is driving up the P_4/Al price ratio. This mechanism is safe (and advantageous) for Spodofos' business case.

Finally, there are options to reduce aluminium costs significantly by also applying aluminium streams, which have a very low yield at smelters. This optimisation is not included in the business case, nor is it factored into the break-even ratio.

There can be no guarantee that the phosphorus-aluminium price ratio will be negative for Spodofos at any given time. The above considerations, history and optimisation possibilities indicate that this is unlikely. The reverse effect, that the business case turns out positive, is more likely.

7

LCA

This chapter contains the integral report of CE Delft: *Klimaatimpact Spodofos, Update 2024*, publication number 24.240402.

SUMMARY

Spodofos is a new technology to recover white phosphorus from the ashes of sewage sludge using aluminium. In addition to white phosphorus, slag and ferrophosphorus are also produced. After simple post-processing, these by-products can be usefully applied. Spodofos is being developed by ThermusP.

CE Delft has determined the climate impact of the Spodofos process. This analysis shows that processing 1 tonne of sewage sludge ash through the Spodofos process has a climate impact of about -1.4 tonnes of CO_2-eq. This is because the products from the Spodofos process, especially the phosphorus, replace conventional products. In addition, all products from the Spodofos process have a lower climate impact than the primary products that they replace.

METHOD

The climate impact of the Spodofos process was determined with a life cycle assessment (LCA). This is an ex-ante LCA, as the process is not yet operational on a large scale.

The LCA was carried out from different perspectives, to answer two questions:

- Waste perspective: what is the climate impact of processing sewage sludge ash with the Spodofos process?
- Product perspective: what is the climate impact of the products (phosphorus, ferrophosphorus and slag) produced by the Spodofos process?

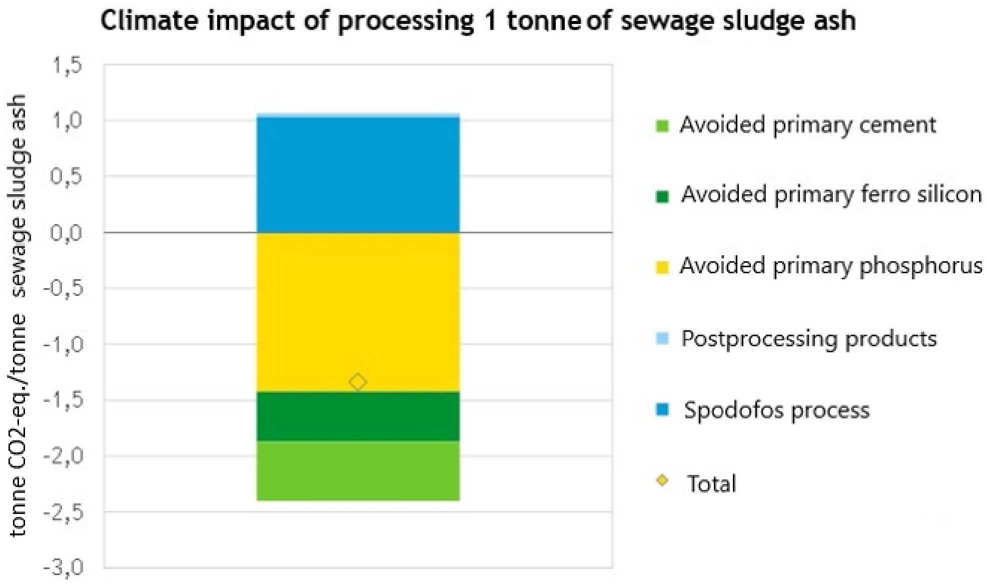
The LCA is based on Spodofos process data supplied by ThermusP. It comes from measurements and calculations based on experiments and represents a processing capacity of 50 kt of sludge ash per year.

RESULTS AND CONCLUSIONS:

WASTE PERSPECTIVE

Figure 28 shows the climate impact of processing 1 tonne of sewage sludge ash through the Spodofos process. The net climate impact of the Spodofos process is calculated at about -1.4 tonne of CO_2-eq. per tonne of sewage sludge ash. The negative result means that greenhouse gas emissions are net avoided by the Spodofos process. This is because the credit for avoided primary products is greater than the climate impact of the Spodofos process itself. The climate impact of the Spodofos process itself is about 1.0 tonne CO_2-eq./tonne sewage sludge ash (dark blue bar). This is mainly due to the use of (secondary) aluminium.

FIGURE 28 CLIMATE IMPACT OF PROCESSING 1 TONNE OF SEWAGE SLUDGE ASH WITH THE SPODOFOS PROCESS, TONNE CO_2-EQ./TONNE SLUDGE ASH



PRODUCT PERSPECTIVE

Table 26 shows the climate impact of the three products from Spodofos in different applications and of the reference products being replaced. The climate impact of the products was determined by distributing the climate impact of the Spodofos process among the three products through economic allocation.

In almost all applications of the three products, the climate impact is lower than the climate impact of the reference product. Only in the case of slag used as insulation material in refractories, the climate impact is comparable to the reference.

TABLE 26 CLIMATE IMPACT OF THE PRODUCTS FROM THE SPODOFOS PROCESS IN DIFFERENT APPLICATIONS, AND THE CLIMATE IMPACT OF THE REFERENCE PRODUCTS, IN TONNE CO2-EQ./TON

Product	Application	Climate impact product		Climate impact reference product
		Maximum[a]	Minimum[a]	
Phosphorus	Primary phosphorus replacement	8.5	4.4	15.1
Ferro-phosphorus	High density medium	1.2	0.7	3.8
	$FeCl_3$ coagulant	0.9	0.7	2.0
Slag	Cement replacement	0.12	0.10	0.5
	Refractory granulate	0.25	0.21	0.5
	Refractory insulation granulate	0.51	0.45	0.5

a) The calculated climate impact depends on the assumed economic value of all outputs from the process (economic allocation). In the table, the highest and lowest values are given.

DISCUSSION

This study has a number of assumptions and limitations:

- This study concerns an ex-ante LCA of the Spodofos process because the process is not yet operational on an industrial scale. In particular, the process data for the expected operation when processing 50 kt of sewage sludge ash is based on a lab-scale/TRL 5 situation when processing 10 kg of sewage sludge ash. We recommend performing the analysis again when data from the scaled-up process is available.
- Spodofos uses secondary aluminium from municipal waste incineration bottom ash. We

calculate its climate impact using the Circular Footprint Formula (CFF) from the EU's Product Environmental Footprint method. The CFF has the advantage that there is a strong incentive for all parties in the chain to keep or make material available for subsequent life cycles in the highest possible quality. Given developments in LCA methodology in Europe, this is a conservative and robust way to calculate the climate impact of secondary aluminium.
- In the analysis from the product perspective, economic allocation is applied to distribute the climate impact of the Spodofos process among the three products. Since the economic value of the products will vary, the actual prices of the co-products should be monitored when Spodofos becomes operational.

7.1 INTRODUCTION

7.1.1 REASON OF THE LCA UPDATE

Spodofos is a new technology to recover white phosphorus from the ashes of sewage sludge using aluminium. In addition to white phosphorus, slag and ferrophosphorus are produced. These by-products can also be usefully applied. ThermusP is the company that develops the Spodofos process.

In 2021, CE Delft conducted an environmental analysis of the Spodofos process. The analysis was incorporated into a STOWA report on the Spodofos process (CE Delft, 2021a). In the meantime, the development of the Spodofos process has continued. More accurate process data are now available and ThermusP has a better understanding of the possible applications for the by-products. The developments of and new insights into the Spodofos process will again be incorporated into a STOWA report.

In this report, we conduct an ex-ante life cycle assessment (LCA) to determine the climate impact of the Spodofos process. We analyse the process from both waste and product perspectives. For the analysis, we use process data derived from measurements and calculations based on experiments for the process with a processing capacity of 50 kt of sludge ash per year. This climate impact analysis will be included in the new STOWA report on Spodofos.

The main changes in the analysis and results compared to the 2021 environmental analysis of the Spodofos process are:
- The new process data have been incorporated into the LCA model. The most important changes in the process data are higher input of aluminium, higher output of phosphorus and ferrophosphorus and use of electricity instead of natural gas in pre-processing the aluminium.
- The climate impact of aluminium inputs has been calculated in a different, more conservative way. This new method is in line with the latest understanding of LCA methods at EU level. The 2021 analysis assumed that post-consumer aluminium from bottom ash had virtually no environmental impact[1]. In the current analysis, we use the principles from the European Circular Footprint Formula to calculate the impact of aluminium. As a result, secondary aluminium has a higher climate impact. This formula also takes into account that the aluminium is converted into alumina in the Spodofos process and is no longer directly recyclable as aluminium.
- We are looking at other applications of ferrophosphorus and slag.

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[1] This study only considered the climate impact of the process by which aluminium is recovered from bottom ash. The aluminium itself was assumed to be environmentally 'free', or available without climate impact.

- The environmental background data have been updated. This has increased the climate impact of some processes (e.g. primary white phosphorus production) and reduced others (e.g. electricity generation).

The 2021 analysis consisted of two parts: a climate impact analysis and a scarcity analysis. In this report, we only analyse climate impact.

7.1.2 READING GUIDE

This report contains the following sections:
Chapter 7.2: provides a description of the methodology used. Among other things, the objectives, approach, functional unit and allocation are covered here.
Chapter 7.3: contains an overview of the data used and details of the modelling. It also describes how the climate impact of secondary aluminium was determined.
Chapter 7.4: this presents and describes the results, both from the analysis from a waste perspective and from the analysis from a product perspective.
Chapter 7.5: herein we discuss the conclusions and limitations of this study.
Annex A contains a data inventory of the additional analysis of the alternative $FeCl_3$ pathway of the Spodofos process.

7.2 METHOD

In this chapter, we describe the purpose, functional unit, approach, allocation, data collection and modelling of this LCA study.

7.2.1 OBJECTIVES

The purpose of this study is to determine the climate impact of the Spodofos process through a life cycle assessment (LCA). The LCA was carried out in accordance with ISO standards 14040 and 14044.

We determine climate impact from two perspectives:

- Waste perspective: what is the climate impact of processing sewage sludge ash with the Spodofos process? The result of this analysis makes comparison with other sewage sludge ash processing methods possible in terms of climate impact.
- Product perspective: what is the climate impact of the products produced using the Spodofos process? The results of this analysis indicate how the products compare with other, conventional production routes.

Table 27 summarises the scope of the analysis and its differences between the waste perspective and product perspective.

TABLE 27 **SUMMARY SCOPE**

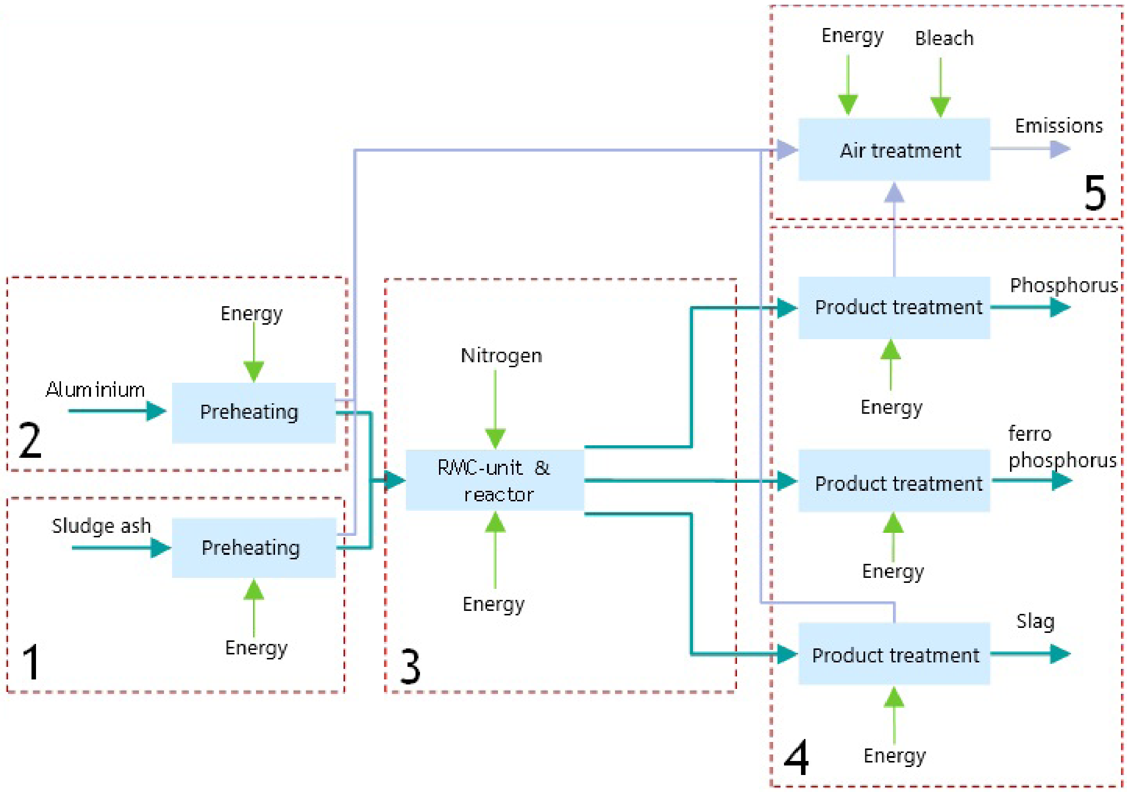
	Waste perspective	Product perspective
Functional unit	Processing 1 tonne sludge ash	Production of 1 tonne phosphorus, 1 tonne slag, 1 tonne ferrophosphorus
Geographic	Netherlands	
Temporal	2024	
Technologic	Processing capacity of 50 kt sludge ash per year	
Modelling	Sludge ash: cut-off (zero climate impact) Aluminium: PEF CFF, refer to paragraph 3.3 Remainder: Ecoinvent, CE Delft	
Multifunctionality	Besides sludge processing (main function), phosphorus, ferrophosphorus and slag are produced. Credits calculated for avoided conventional production of phosphorus, ferrosilicon and slag	Phosphorus, ferrophosphorus and slag are co-products. Economic allocation was applied to distribute climate impact. Allocation factor based on economic value in different applications
Indicator	Climate impact	
Additional analyses	1 Alternative application for ferrophosphorus and slag 2 Renewable electricity 3 Heat recovery and reuse 4 Aluminium composition	N/A

Further applications of the products from the Spodofos process are beyond the scope of this analysis.

7.2.2 TECHNOLOGY DESCRIPTION

In the Spodofos process, aluminium is used to recover phosphorus from sludge ash. By-products are ferro phosphorus and slag. The process can be divided into five sub-processes, as shown in Figure 29. In this analysis, we assume a processing capacity of 50 kt of sludge ash per year. Per tonne of sludge ash, 94 kg of phosphorus, 119 kg of ferrophosphorus and 1,024 kg of slag are produced.

FIGURE 29 **SCHEMATIC OVERVIEW OF THE PROCESS**



1. Pretreatment of sludge ash
   Before the sludge ash is mixed with the aluminium, it is heated to a temperature of (max) 700°C.

2. Preparation of aluminium
   In the Spodofos process, aluminium is used to recover phosphorus. ThermusP assumes the use of aluminium recovered from bottom ash from waste incineration.
   Depending on the phosphorus concentration in the sludge ash and other variables, a calculated amount of aluminium is added. This aluminium is heated to a temperature of about 700°C.

3. RMC unit and reactor
   In the Reaction Mixture Conditioning unit (RMC), the correct amounts of ash and aluminium are brought together, and the aluminium is dispersed in the ash.
   The reaction mixture of the aluminium and ash is dosed into the reactor via a dosing buffer. The dosing buffer is maintained at slight overpressure relative to the reactor using nitrogen. In the reactor, a reaction takes place where phosphorus gas, liquid slag and liquid ferrophosphorus are formed without the addition of external energy.

4. Product treatment
   Through a separation vessel, the ferrophosphorus flows into moulds and the slag into a slag bath. The slag is quenched with water, causing it to solidify rapidly to its expanded form.
   The phosphorus gas is condensed into liquid phosphorus, which is, after filtration, stored as the final product in a tank under a layer of water.

5. Air and waste treatment
   The process creates three air streams that need to be treated. The flue gases from the ash and aluminium heaters are cleaned of dust and some volatilised components. A bleach leach wash is used to wash phosphorus from the non-condensable gases in the phosphorus condensation. Finally, the ventilation air from the slag processing is cleaned of hydrogen sulphide with an alkaline scrubber.

7.2.3 DELINEATION

7.2.3.1 SYSTEM BOUNDARIES AND FUNCTIONAL UNIT

The Spodofos process is analysed from two perspectives: a waste perspective (the processing of sludge ash with Spodofos) and a product perspective (the production of different products with Spodofos). The two perspectives have different system boundaries and functional units. These are discussed below.

WASTE PERSPECTIVE

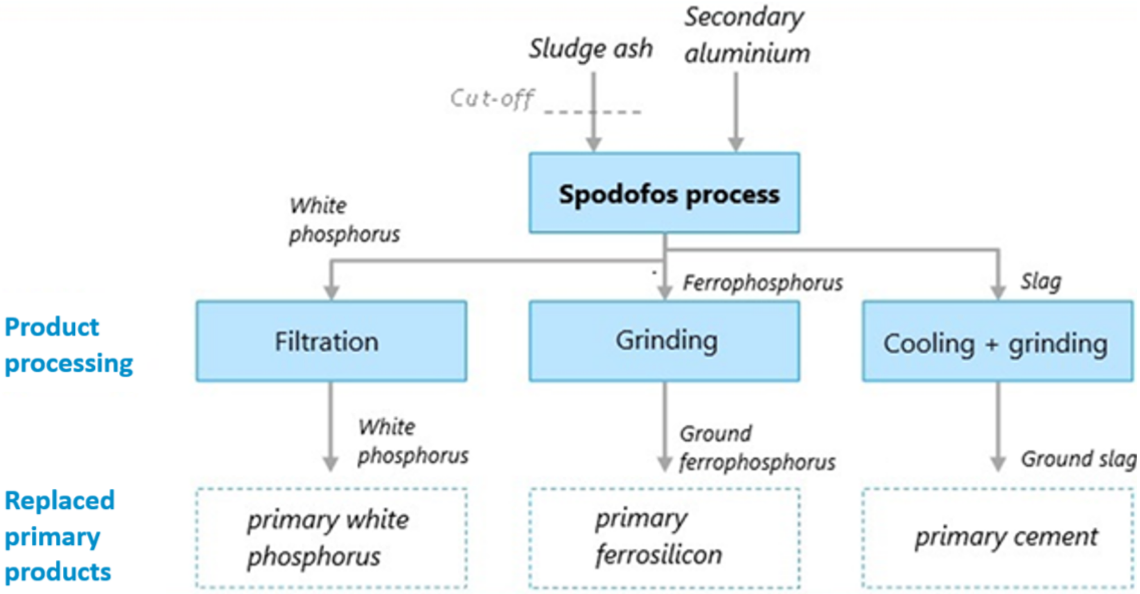
Figure 30 shows the system boundaries of the basic analysis[2] from the waste perspective.

The functional unit of this analysis is the processing of 1 tonne of sludge ash.

The starting point of the analysis is sludge ash from sewage sludge incineration. For the composition of the sludge ash processed in the Spodofos process, we assume a weighted average of SNB and HVC incineration ashes. This ash contains 10.1% phosphorus. Sludge ash is a waste product and is used as filler in salt mines. For this reason, the processing steps to arrive at the sludge ash are outside the scope of this analysis and its climate impact is not included.

The Spodofos process produces white phosphorus, ferrophosphorus, and slag from the sludge ash and aluminium. For the waste perspective, based on outlets and prices, these products were chosen to replace the primary production of white phosphorus, ferrosilicon (15%), and cement (substitution method).

FIGURE 30 SYSTEM BOUNDARIES OF THE ANALYSIS FROM A WASTE PERSPECTIVE



In addition to the basic analysis, we also conduct an analysis for alternative uses of the products from the Spodofos process. See Section 7.2.5.

PRODUCT PERSPECTIVE

Figure 31 shows the system boundaries of the analysis from a product perspective.

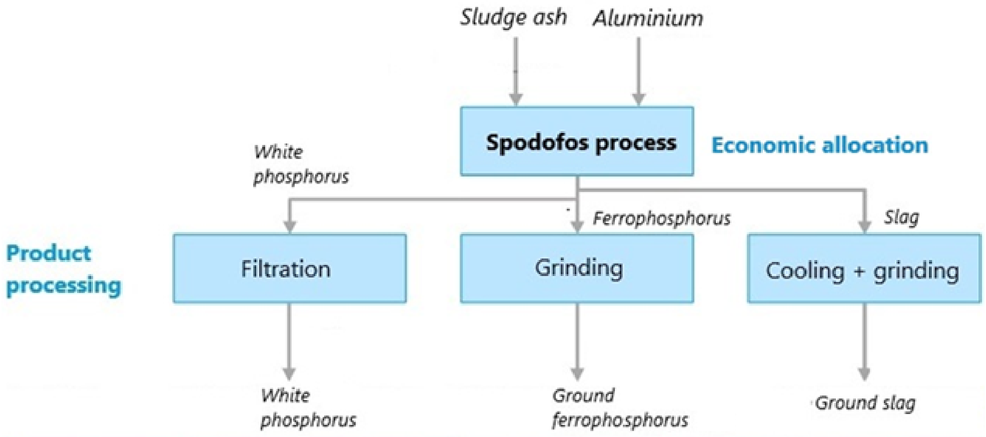
The functional unit of this analysis is the production of 1 tonne of white phosphorus, 1 tonne of ferrophosphorus or 1 tonne of slag.

Again, the starting point of this analysis is sludge ash from the incineration of sewage sludge containing 10.1% phosphorus. As mentioned before, the climate impact of the production of sewage sludge ash is not included in this analysis.

We apply economic allocation to divide the climate impact of the Spodofos process among its three products (white phosphorus, ferrophosphorus, and slag). We then add the climate impact of the processing step. The economic value of the products depends on the application and the product(s) they replace.

The product perspective analysis compares the climate impact of products from the Spodofos process with the climate impact of primary products replaced by Spodofos products.

FIGURE 31 SYSTEM BOUNDARIES OF THE ANALYSIS FROM A PRODUCT PERSPECTIVE



We look at different applications of the three products from the Spodofos process in the product perspective analysis. Table 28 shows how those different applications are combined and the price calculated for that product in each respective application.

TABLE 28 COMBINATIONS OF PRODUCT APPLICATIONS IN THE ANALYSIS FROM A PRODUCT PERSPECTIVE

Analysis	Product	Replaced product	Product price (€/tonne)	Allocation factor
Basic analysis	White phosphorus	White phosphorus	3,650	79%
	Ferrophosphorus	Ferrosilicon (15%)	500	12%
	Slag	Cement	40	9%
Additional ferrophosphorus	White phosphorus	White phosphorus	3,650	65%
	Ferrophosphorus	$FeCl_3$	230	27%
	Slag	Cement	40	7%
Additional slag 1	White phosphorus	White phosphorus	3,650	66%
	Ferrophosphorus	Ferrosilicon (15%)	500	10%
	Slag	Chamotte (granulate)	130	23%
Additional slag 2	White phosphorus	White phosphorus	3,650	44%
	Ferrophosphorus	Ferrosilicon (15%)	500	7%
	Slag	Chamotte (insulation)	400	49%

The production of capital goods such as the process plants themselves is not included in the analysis. This is common in LCAs of industrial processes, as the environmental impact of capital goods is usually very small compared to other factors (such as energy use and the impact of resources).

The allocation factor is the fraction of the product's yield relative to the summed yields of all products per tonne of sludge ash.

7.2.3.2 GEOGRAPHICAL, TECHNOLOGICAL AND TIME DEMARCATION

In the analysis, we use the following geographical location and time demarcation:

- Geographical location: We are looking at processing sludge ash with the Spodofos process in the Netherlands. This means we assume the Dutch electricity mix and low-calorific natural gas. For the products avoided, we assume average European or global production processes.
- Technological delineation: The process data apply to a Spodofos plant with a processing capacity of 50 kt of sludge ash per year (containing 10.1% phosphorus).
- Timeframe: The analysis focuses on the climate impact of sludge ash processing around 2024. The climate impact of the underlying processes, such as electricity production, has

been determined for this period. Future changes in the underlying systems may mean that the climate impact as currently calculated will no longer be up to date by then.

7.2.4 DATA AND MODELLING

The data used were obtained from ThermusP and based on literature. ThermusP determined the process data based on TRL 5 testing and calculations. The text box below contains an explanation from ThermusP on the determination of the process data.

> **BOX 1 - THERMUSP EXPLANATION OF PROCESS DATA**
>
> The process data used are based on the mass balance derived from the experiments in TRL 5. Given the strong improvement, without any optimisation, of the phosphorus content in the ferrophosphorus compared to ferrophosphorus from traditional furnaces, the mass balance has been tuned to a feasible phosphorus content of 5% at higher silicon content. The other process data are in line with the calculations in the STOWA 2021-57 feasibility study with some modifications: use of lower grade aluminium, use of the maximum preheat temperature (700°C instead of 600°C), inductive heating of the aluminium, and solidification of the slag in a slag bath. The heat content of molten slag at the reaction temperature was determined experimentally by quenching in a water bath.

The process data used in this analysis can be found in Chapter 7.3.
For most environmental background data, we used the LCA database ecoinvent (Version 3.10). In addition, datasets developed by CE Delft were used for some background processes. The processes were modelled in the LCA software SimaPro (Version 9.6). In SimaPro, the foreground data on the Spodofos process are linked to the environmental background data. The climate impact was calculated using the IPCC 2021 GWP100 methodology (Version 1.03).

7.2.5 ADDITIONAL ANALYSES

Besides the basic analyses from waste perspective and product perspective, the study also contains additional analyses. These were carried out only for the waste perspective. The additional analyses comprise of the following:

- Alternative applications: The ferrophosphorus and slag from the Spodofos process can replace several primary products. In this additional analysis, we look at the climate impact of the Spodofos process when slag is used in refractory granules, replacing calcined chamotte.
- Renewable electricity: It is possible to fully electrify the Spodofos process. Electricity would be used for pre-processing the sludge ash instead of natural gas. In addition, we assume in this additional analysis that all electricity used in the Spodofos process is renewable.
- Heat recovery: When cooling the slag, heat can be recovered. This amounts to 2,340 MJ of heat per tonne of sludge ash. In this additional analysis, we look at the effect on climate impact if this heat can be put to good use, replacing natural gas combustion. We assume a further 25% loss when the heat is transported.
- Aluminium composition: In the basic analysis, we assume the input of secondary aluminium from bottom ash with an aluminium content of 88%. It is technically possible to blend in low-grade aluminium from bottom ash with an aluminium content of 20%, replacing some of the higher-grade secondary aluminium. In this additional analysis, we look at the effect of applying 20% low-grade secondary aluminium (with an aluminium content of 20%) and 80% high-grade secondary aluminium (with an aluminium content of 88%). We assume that the low-grade aluminium is a waste product and thus has virtually no economic value.

The results are discussed in Sections 7.4.1.2 to 7.4.1.5.

7.3 INVENTORY

7.3.1 PROCESS DATA BASIC ANALYSIS

Table 29 summarises all data for the Spodofos process. It can be noted here that the data used are based on tests and calculations and therefore less certain than data from an operational plant.

TABLE 29 SPODOFOS PROCESS DATA INVENTORY, PER TONNE OF SLUDGE ASH

	Unit	Quantity	Comments and modelling Ecoinvent processes in italics
Preprocessing of sludge ash			
Sludge ash	kg	1,000	Zero climate impact
Electricity	kWh	5.1	Average Dutch electrical mix in 2022 (CE Delft, 2023)
Natural gas	Nm^3	24	Production: Natural gas, high pressure {NL}| marketable Combustion: 1.78 kg CO_2/Nm^3 (RVO, 2024)
Preprocessing of aluminium			
Aluminium	kg	269	Input is secondary aluminium with an aluminium content of 88%. The amount of pure aluminium totals 237 kg. 20% Aluminium scrap, post-consumer, prepared for melting {RER}| treatment of aluminium scrap, post-consumer by collecting, sorting, cleaning, pressing 39% Aluminium, primary, ingot {IAI Area, EU27 & EFTA} marketable See Section [] for more information.
Electricity	kWh	87	See preprocessing of sludge ash
RMC-unit and -reactor			
Nitrogen	kg	2	Nitrogen, atmospheric and 0.21 kWh electricity/kg N for production (Parker Hannifin Corporation, 2013)
Electricity	kWh	28	See preprocessing of sludge ash
Product processing			
Electricity	kWh	2	See preprocessing of sludge ash
Slag treatments	kg	1,026	SBK Crushing mineral materials MRPI (NMD 3,9), climate impact equals 0.0015 kg CO2-eq./kg
Diesel	litre	1.4	Diesel, burned in building machine {GLO}| marketable Combustible value: 43.2 MJ/kg (RVO, 2024); Density: 0.84 kg/litre (Wikipedia, 2021)
Cooling liquids	litre	750	Water, cooling, unspecified natural origin, NL
Air and waste treatments			
Electricity	kWh	8	See preprocessing of sludge ash
Water	litre	750	Water, completely softened {RER}| marketable
Caustic soda (35%)	kg	0.5	Sodium hydroxide, without water, in 50% solution state {RER}| Marketable Corrected for content
Bleach (12.5%)	kg	1	Sodium hypochlorite, without water, in 15% solution state {RER}| Marketable Corrected for content
Copper sulphate	g	6	Copper sulphate {GLO}| marketable
Dust for landfill	kg	30	Inert waste {RER}| treatment of inert waste, sanitary landfill
Outputs			
Phosphorus	kg	94	To processing, refer to paragraph 7.3.2
Ferrophosphorus	kg	119	To processing, refer to paragraph 7.3.2
Slag	kg	1,026	To processing, refer to paragraph 7.3.2

7.3.2 REPROCESSING PRODUCTS AND AVOIDED PRODUCTS

PHOSPHORUS

The white phosphorus from the Spodofos process must be filtered. No energy or materials are required for this reprocessing step. After the filtration step, the white phosphorus can be sold.

The economic value of the product will total around €3.650 per tonne.

The phosphorus produced is chemically similar to conventional white phosphorus. We therefore assume that the climate impact avoided by using Spodofos phosphorus is that of conventional white phosphorus. White phosphorus is currently produced in the United States, China, Kazakhstan, and Vietnam. The 2021 analysis assumed that phosphorus produced in the Spodofos process will replace white phosphorus sourced from Kazakhstan (50%) and Vietnam (50%). This assumption is reused here. The white phosphorus produced will be used in Europe, and so the transport of conventional white phosphorus from Kazakhstan (by train) and Vietnam (by cargo ship) to Europe will also be avoided. Table 30 shows how the primary production of white phosphorus has been modelled.

TABLE 30 MODEL OF AVOIDED PRIMARY PRODUCTION OF 1 TONNE OF WHITE PHOSPHORUS

	Unit	Quantity	Comments and modelling Ecoinvent processes in italics
White phosphorus	ton	1	Phosphorus, white, liquid {RoW}| phosphorus production
Transport by train	tkm	50% * 5,000	5,000 km, medium diesel train (CE Delft, 2021b)
Transport by freighter	tkm	50% * 17,650	17,650 km, bulk carrier (CE Delft, 2021b)

FERROPHOSPHORUS

The ferrophosphorus from the Spodofos process has several probable applications. These applications differ in required reprocessing steps, economic value of the ferrophosphorus and avoided products. Table 31 lists these factors for the different applications considered in this study.

In the basic analysis, we look at application of ferrophosphorus as a high-density medium in sink-float separation. It would replace ferrosilicon with silicon content of 15%. The environmental background data database only contains a dataset for production of ferrosilicon with 72% silicon content. The production process for 15% ferrosilicon was manually modelled based on literature using the dataset for 72% ferrosilicon as input (Schmitz & Trauzeddel, 2016); see Table 31.

It is also possible to convert ferrophosphorus into $FeCl_3$ (38%) and calcium phosphate. The calcium phosphate could be fed back into the Spodofos process to increase white phosphorus production. In this route, all process data from the Spodofos process change. The data inventory for this route can be found in Table 34 in Appendix A. The energy and raw materials required to produce $FeCl_3$ and calcium phosphate from ferrophosphorus are shown below in Table 31 and in more detail in Appendix A, Table 34. This $FeCl_3$ pathway is only included in the analysis from a product perspective.

TABLE 31 **POSSIBLE USES OF FERROPHOSPHORUS, WITH REPROCESSING INPUTS, ECONOMIC VALUE AND PRIMARY PRODUCT AVOIDED, PER TONNE OF FERROPHOSPHORUS**

Analysis	Application	Inputs for processing (per tonne of ferro phosphorus)	Economic value (€/tonne)	Product avoided
Basic analysis	High-density medium in sink-float separation	Electricity: 40 kWh	500	1 tonne Ferrosilicon 15% Modelled as: 0.21 tonne Ferrosilicon {GLO}| marketable 0.79 tonne Steel, unalloyed {GLO}|marketable 500 kWh Electricity, high voltage {GLO}| marketable (Schmitz & Trauzeddel, 2016) 1 tonne Ferrosilicium 15%
Additional analysis	Production of $FeCl_3$ (38%) coagulant	Electricity: 25 kWh Natural gas: 140 Nm^3 Slaked lime: 580 kg Soda: 770 kg Hydrochloric acid (30%): 5,200 kg Slaked lime: 580 kg Soda: 770 kg Hydrochloric acid (30%): 5,200 kg	230 (per tonne $FeCl_3$)	0.95 tonne of $FeCl_3$ (40%), modelled as: 0.38 tonne Iron(III) chloride, without water, in 40% solution state {GLO}|marketable

SLAG

The slag from the Spodofos process can be applied in several ways. These applications differ in required reprocessing steps, economic value of the slag and avoided products. Table 32 summarises these factors for the different applications considered in this study.

In the basic analysis, we look at the application of slag as a cement substitute. This requires the slag to be finely ground. In the supplementary analysis, we also include the application of slag as granulate in refractories (as a replacement for calcined chamotte) and as insulation material in refractories (as a replacement for expanded chamotte). For the climate impact of calcined chamotte and expanded chamotte, we use the same source, as no separate climate impacts are available for these materials.

If the slag can be applied as insulation material in refractory material, the economic value of the slag increases significantly compared to its application as granules in refractory material.

TABLE 32 **POSSIBLE USES OF SLAG, WITH REPROCESSING INPUTS, ECONOMIC VALUE AND PRIMARY PRODUCT AVOIDED, PER TONNE OF SLAG**

Analysis	Inputs for processing (per tonne of slag)	Application	Economic value (€/tonne)	Product avoided
Basic analysis	Electricity: 80 kWh	Cement substitution	40	1 tonne Cement, CEM IV/B {Europe without Switzerland}|marketable
Additional analysis	Electricity: 10 kWh	Granulate in refractories	130	1 tonne of calcined chamotte with a climate impact of 0.513 kg CO_2-eq./kg (Imerys, 2021)
Additional analysis	Electricity: 10 kWh	Insulation granulate in refractories	400	1 tonne of calcined lightweight chamotte with a climate impact of 0.513 kg CO_2-eq./kg (Imerys, 2021)

7.3.3 CLIMATE IMPACT ALUMINIUM INPUT

In the Spodofos process, aluminium from bottom ash derived from waste incineration is used as input material. This aluminium is oxidised in the process to alumina which ends up in the slag.

In the 2021 analysis, the calculation of the climate impact of aluminium from bottom ash only included the impact of recovering the aluminium.

This method of calculation did not take into account the aluminium lost in the Spodofos process, and additional primary aluminium must be produced elsewhere to meet the increased demand for aluminium.

Since 2021, there have been major developments around the methodology of calculating and attributing the environmental impact of secondary materials. The European Commission has developed the Product Environmental Footprint (PEF). This methodology ensures more uniform and comparable LCAs.

Part of the PEF method is the Circular Footprint Formula (CFF), see Equation 1. The CFF can be used to calculate the environmental impact of both the input of materials for production, and the processing of these materials at the end of a product's lifecycle. The benefit of recycling materials is divided between the party that inputs recycled materials and the party that ensures that recycled materials become available again at end-of-life.

The second part of the formula (with the blue box) gives the environmental impact of inputs of secondary material. We use this part of the formula to calculate the climate impact of aluminium from bottom ash.

EQUATION 1 **FULL CIRCULAR FOOTPRINT FORMULA (CFF) FROM PEF METHOD (EC, 2021)**

Material

$$(1-R_1)E_V + \boxed{R_1 \times \left(A \times E_{recycled} + (1-A)E_V \times \frac{Q_{Sin}}{Q_p}\right)} + (1-A)R_2 \times \left(E_{recyclingEoL} - E_V^* \times \frac{Q_{Sout}}{Q_P}\right)$$

Energy

$$(1-B)R_3 \times (E_{ER} - LHV \times X_{ER,heat} \times E_{SE,heat} - LHV \times X_{ER,elec} \times E_{SE,elec})$$

Disposal

$$(1-R_2-R_3)E_D$$

In equation 2, only the blue framed part from equation 1 is shown, with the names of variables adjusted.

EQUATION 2 **FORMULA FOR CALCULATING CLIMATE IMPACT OF RECYCLED INPUT MATERIAL**

$$E_{recycled\ input} = R_1 * A * E_{recycled\ material} + (1-A) * E_{primary\ material} * \frac{Q_{Sin}}{Q_p}$$

In the case of aluminium from bottom ash:

- R_1 is the proportion of recycled material used. In the case of the Spodofos process, 100% of the aluminium input comes from bottom ash, so the value of R1 is 1.
- $E_{recycled}$ input is the climate impact of the aluminium from bottom ash used in the Spodofos process.
- A is the allocation factor by which the impact and benefit of recycled material is shared between the user and supplier of the recycled material. For aluminium, A has the value 0.2 (EC, 2022).
- $E_{recycled\ material}$ is the climate impact of recycling aluminium from bottom ash.
- $E_{primary\ material}$ is the climate impact of primary aluminium.
- Q_{Sin} is the quality of aluminium from bottom ash.
- Q_p is the quality of primary aluminium.

- The quality factors $Q_S$in and Qp are determined based on the economic value of both materials. For primary aluminium (Qp) we assume a price of €2,350 per tonne of aluminium, for aluminium from bottom ash ($Q_S$in) we assume a price of €1,136 per tonne of aluminium (€1,000 per tonne of aluminium from bottom ash with an aluminium content of 88%).

The climate impact of the recycled inputs then becomes:

EQUATION 3 SIMPLIFIED FORMULA FOR CALCULATING CLIMATE IMPACT OF ALUMINIUM FROM BOTTOM ASH

$$E_{recycled\ input} = 0.2 * E_{recycled\ material} + 0.39 * E_{primary\ material}$$

7.4 CLIMATE IMPACT RESULTS

In this section, we present the results of the LCA of the Spodofos process.

Section 7.4.1 contains the results of the analysis from a waste perspective, and Section 7.4.2 contains the results of the analysis from a product perspective.

7.4.1 WASTE PERSPECTIVE: PROCESSING SLUDGE ASH

7.4.1.1 BASIC ANALYSIS

Figure 32 shows the climate impact of processing 1 tonne of sludge ash with the Spodofos process including the credits for avoided products. The climate impact of the Spodofos process itself is shown with the dark blue bar. On top of that there is a small climate impact of the reprocessing of the products (in light blue). The part of the bar below the x-axis shows the avoided climate impact as the products from the Spodofos process replace primary products.

The net climate impact of the Spodofos process comes out to about -1.4 tonne of CO_2-eq. per tonne of sludge ash. The negative climate impact means that greenhouse gas emissions are net avoided by the Spodofos process. This is because the credit for avoided primary production is greater than the climate impact of the Spodofos process itself.

In particular, the credit for saved primary phosphorus is significant. This is due to the high climate impact of primary phosphorus production (about 15 tonnes of CO_2-eq./tonne phosphorus).

The credits for saved primary ferrosilicon and saved primary cement are similar. Primary ferrosilicon has a higher climate impact than primary cement, but a much larger amount of cement is replaced.

FIGURE 32 CLIMATE IMPACT OF PROCESSING 1 TONNE OF SLUDGE ASH WITH THE SPODOFOS PROCESS (WITH BENEFIT FOR AVOIDED PRODUCTS), IN TONNE CO_2-EQ./TONNE SLUDGE ASH

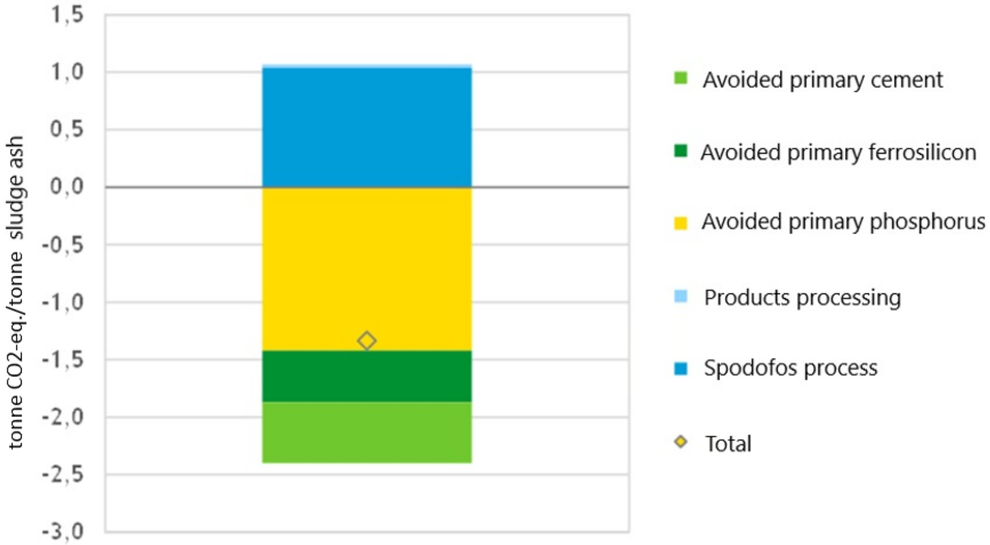


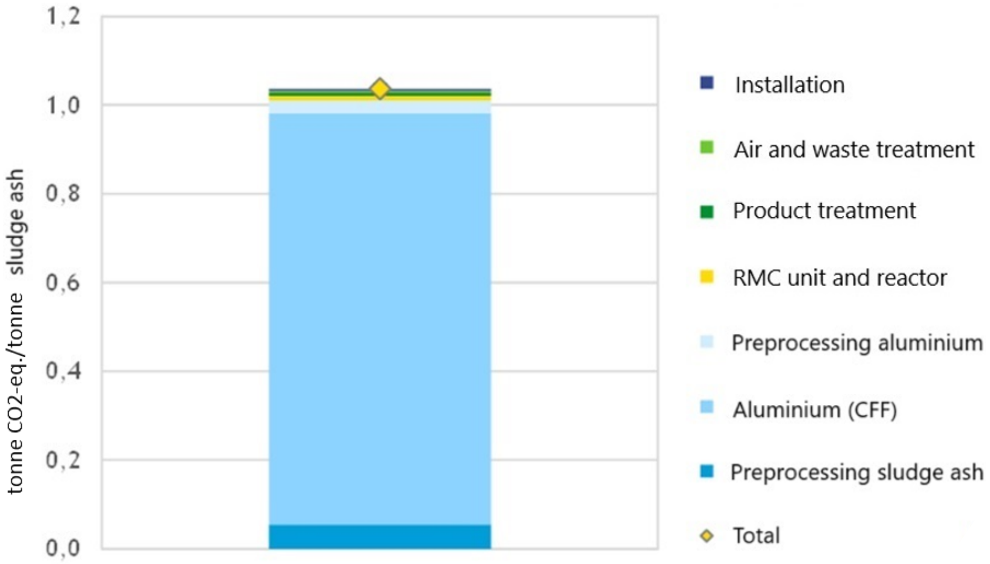
Figure 33 shows the climate impact of the Spodofos process alone, excluding reprocessing and credits for saved products. The climate impact is broken down into the different process steps that make up the Spodofos process.

The climate impact of the Spodofos process itself is about 1.0 tonne of CO_2-eq./tonne of sludge ash. There is a small margin of error on the results (0.01 tonne of CO_2-eq./tonne sludge ash) due to uncertainty in the inputs, but this is not reflected in the graph.

The climate impact is mainly caused by the pre-processing of aluminium.

The climate impact of this process consists of the impact of aluminium (97%) and the impact of electricity (3%). The aluminium input has a large influence on the total climate impact because part of the impact of primary aluminium production is allocated to secondary aluminium from bottom ash (see Section 7.3.3 for explanation).

FIGURE 33 CLIMATE IMPACT OF PROCESSING 1 TONNE OF SLUDGE ASH WITH THE SPODOFOS PROCESS (WITHOUT BENEFIT FOR AVOIDED PRODUCTS), IN TONNES OF CO_2-EQ./TONNE SLUDGE ASH

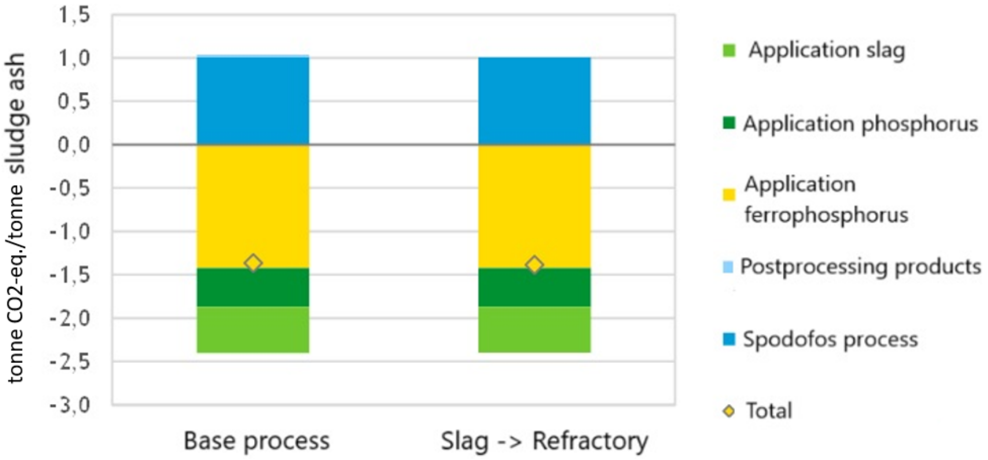


7.4.1.2 ADDITIONAL ANALYSIS: ALTERNATIVE USES

In this additional analysis, we look at the climate impact of the Spodofos process at applying slag in refractory granules, replacing calcined chamotte.

Figure 34 shows the climate impact of this analysis. When applying slag in refractories (right bar), the climate impact of the Spodofos process is about -1.4 tonne of CO_2-eq. per tonne of sludge ash. The credit for saved primary product when slag is applied remains approximately the same, as the climate impact of producing calcined chamotte (0.5 kg CO_2-eq./kg) is similar to the climate impact of cement production (0.5 kg CO_2-eq./kg).

FIGURE 34 CLIMATE IMPACT OF PROCESSING 1 TONNE OF SLUDGE ASH WITH THE SPODOFOS PROCESS FOR AN ALTERNATIVE USE OF SLAG, IN TONNES OF CO_2-EQ./TONNE OF SLUDGE ASH



7.4.1.3 ADDITIONAL ANALYSIS: RENEWABLE ELECTRICITY

With full electrification of the Spodofos process and the use of renewable electricity for all process steps, the climate impact of the Spodofos process decreases per tonne of sludge ash from 1.04 tonne CO2-eq. to 0.96 tonne CO_2-eq.. The total climate impact, including avoided primary products, therefore decreases from -1.36 tonne CO_2-eq. to -1.42 tonne CO_2-eq. per tonne of sludge ash.

7.4.1.4 ADDITIONAL ANALYSIS: HEAT RECOVERY

If heat is recovered from the slags and this heat avoids the burning natural gas, this yields an additional avoided climate impact per tonne of sludge ash of -0.12 tonne CO_2-eq. This brings the total climate impact to -1.49 tonne CO_2-eq..

7.4.1.5 ADDITIONAL ANALYSIS: COMPOSITION OF ALUMINIUM INPUTS

When using low-grade secondary aluminium, the climate impact of the aluminium input decreases per tonne of sludge ash from 0.93 tonne CO_2-eq. to 0.89 tonne CO_2-eq.. In addition, slag production and thus the avoided primary production of cement also increases. As a result, the total climate impact of the Spodofos process including avoided primary production decreases per tonne of sludge ash from -1.36 tonne CO_2-eq. to -1.42 tonne CO_2-eq..

7.4.2 PRODUCT PERSPECTIVE: PRODUCTION OF PHOSPHORUS, FERROPHOSPHORUS AND SLAG

In the analysis from a product perspective, we calculated the climate impact of the various outputs produced by the Spodofos process. The climate impact of the Spodofos process is divided among its products by means of economic allocation. As a result, the products' climate impact depends on their economic value, which in turn depends on their applications. The economic allocation factors applied are discussed in Table 28.

In the subsections below, we discuss the climate impact per product for different applications.

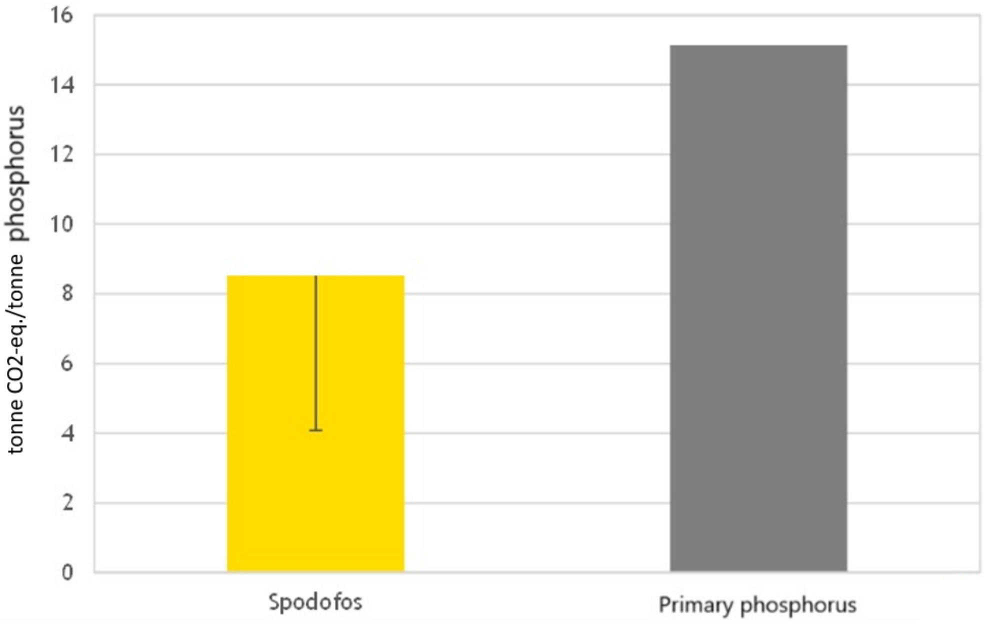
7.4.2.1 PHOSPHORUS PRODUCT

Figure 35 shows the climate impact of 1 tonne of white phosphorus produced with Spodofos and 1 tonne of primary white phosphorus. The yellow bar shows the climate impact of white phosphorus from the Spodofos process as calculated in the basic analysis: ferrophosphorus then replaces ferrosilicon and slag replaces cement. The climate impact of white phosphorus is about 8.5 tonne of CO_2-eq./tonne.

The spread at Spodofos indicates how the climate impact of white phosphorus changes with other uses of ferrophosphorus and slag. With a higher economic value of ferrophosphorus and slag, a smaller proportion of the climate impact of the Spodofos process is attributed to white phosphorus. The climate impact of white phosphorus is lowest (4.4 tonne CO_2-eq./tonne) in the $FeCl_3$ route, where ferrophosphorus is converted into $FeCl_3$ and the slag is applied as refractory insulation material.

In all scenarios, white phosphorus from Spodofos has a significantly lower climate impact than primary white phosphorus (about 15 tonne CO_2-eq./tonne).

FIGURE 35 **CLIMATE IMPACT OF WHITE PHOSPHORUS PRODUCED WITH THE SPODOFOS PROCESS AND PRIMARY WHITE PHOSPHORUS, IN TONNE CO_2-EQ./TONNE PRODUCT**



7.4.2.2 FERROPHOSPHORUS PRODUCTS

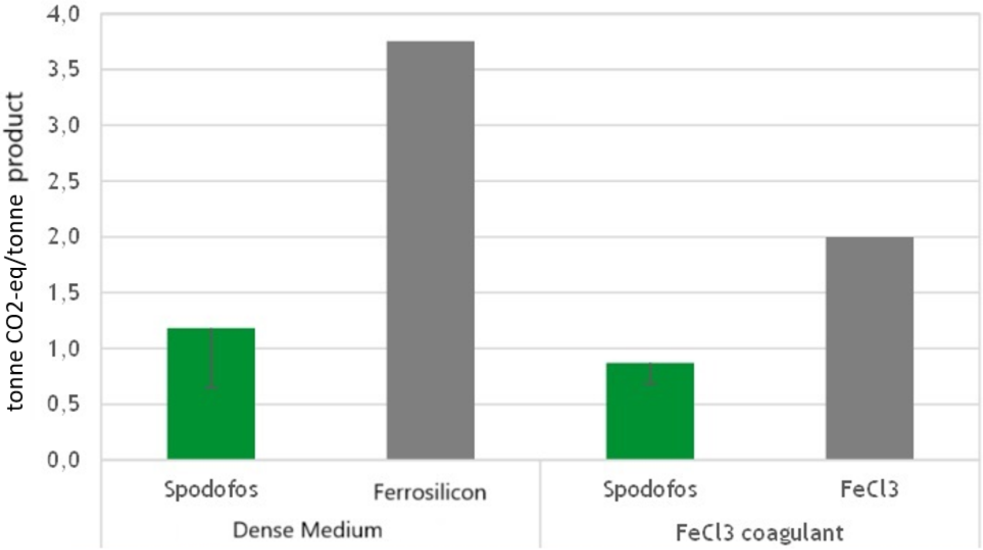
Figure 36 shows the climate impact of ferrophosphorus from Spodofos in three different applications (in dark green), along with the primary product being replaced (in grey).

When ferrophosphorus is used as a high-density medium in sink-float separation, the climate impact is between 1.2 tonne CO_2-eq./tonne (baseline analysis) and 0.7 tonne CO_2-eq./

tonne (when slag is used as a refractory insulation material). This climate impact is lower than the climate impact of the primary ferrosilicon replaced in this application (3.8 tonne CO_2-eq./tonne).

When reprocessing ferrophosphorus to $FeCl_3$, the climate impact of the $FeCl_3$ from the Spodofos process is between 0.9 tonne CO_2-eq./tonne (baseline analysis) and 0.7 tonne CO_2-eq./tonne (when slag is used as refractory insulation material). This climate impact is lower than the climate impact of primary $FeCl_3$ replacement (2.0 tonne CO_2-eq./tonne).

FIGURE 36 **CLIMATE IMPACT OF FERROPHOSPHORUS PRODUCTS PRODUCED WITH THE SPODOFOS PROCESS AND PRIMARY REFERENCE PRODUCTS, IN TONNE CO_2-EQ./TONNE PRODUCT**



7.4.2.3 SLAG PRODUCTS

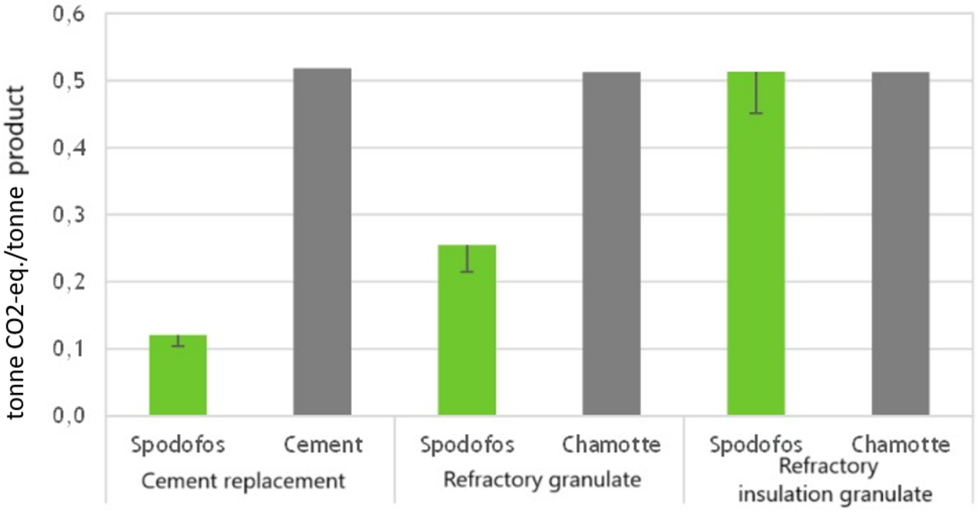
Figure 37 shows the climate impact of slag from Spodofos in three different applications (in light green), along with the primary product being replaced (in grey).

When slag is used as a cement substitute, the climate impact of slag is about 0.1 tonne CO_2-eq./tonne. In this case, the different applications of ferrophosphorus have little impact on the climate impact of slag. The climate impact of the slag is lower than the climate impact of the cement being replaced (0.5 tonne CO_2-eq./tonne).

When using slag as refractory granulate, the climate impact of slag is about 0.2 tonne CO_2-eq./tonne. Again, the climate impact of the slag is lower than the climate impact of the chamotte being replaced (0.5 tonne CO_2-eq./tonne).

If the slag is used as refractory insulation material, the climate impact is about 0.5 tonne CO_2-eq./tonne. In this case, the climate impact of the slag is comparable to the climate impact of the product being replaced (0.5 tonne CO_2-eq./tonne). For the product to be replaced, this is a conservative assumption. It is also possible that slag replaces high-quality chamotte, which has a climate impact of about 1.0 tonne CO_2-eq./tonne.

FIGURE 37 **CLIMATE IMPACT OF SLAG PRODUCTS PRODUCED WITH THE SPODOFOS PROCESS AND PRIMARY REFERENCE PRODUCTS, IN TONNE CO_2-EQ./TONNE PRODUCT**



7.5 DISCUSSION AND CONCLUSION

This ex-ante LCA determines the climate impact of the Spodofos process from two perspectives:

- Waste perspective: what is the climate impact of processing sludge ash with the Spodofos process? The results of this analysis can be used to determine whether the Spodofos technology offers an advantage in terms of climate impact compared to other sludge ash processing methods.
- Product perspective: what is the climate impact of the products (phosphorus, ferrophosphorus and slag) produced by the Spodofos process? The results of this analysis indicate how the products compare with other, conventional production routes.

7.5.1 CONCLUSIONS

WASTE PERSPECTIVE

The climate impact of processing sludge ash with the Spodofos process is about -1.4 tonne of CO_2-eq./tonne sludge ash. The climate impact consists of the impact of the Spodofos process (1.0 tonne of CO_2-eq./tonne sludge ash) and the avoided impact by replacing primary products (-2.4 tonne of CO_2-eq./tonne sludge ash). In particular, the production of phosphorus and thereby avoiding primary phosphorus contributes a lot to the avoided climate impact.

PRODUCT PERSPECTIVE

Table 33 shows the climate impact of the three products from Spodofos in different applications and of the reference products they replace. The climate impact of the products was determined by distributing the climate impact of the Spodofos process among the three products through economic allocation. The climate impact of the products therefore depends on the economic value of all three products. If the economic value of one of the products changes due to a different application, the climate impact of all three products changes. Hence, maximum and minimum climate impacts are shown for each product.

In almost all applications of the three products, the climate impact is lower than the climate impact of the reference product. Only in the case of slag used as refractory insulation material is the climate impact comparable to that of the reference product.

TABLE 33 **CLIMATE IMPACT OF THE PRODUCTS FROM THE SPODOFOS PROCESS IN DIFFERENT APPLICATIONS, AND THE CLIMATE IMPACT OF THE REFERENCE PRODUCTS, IN TONNE CO_2-EQ./TONNE**

Product	Application	Climate impact product		Climate impact reference product
		Maximum	Minimum	
Phosphorus	Primary phosphorus replacement	8.5	4.4	15.1
Ferro-phosphorus	High density medium	1.2	0.7	3.8
	$FeCl_3$ coagulant	0.9	0.7	2.0
Slag	Cement replacement	0.12	0.10	0.5
	Refractory granulate	0.25	0.21	0.5
	Refractory insulation granulate	0.51	0.45	0.5

The calculated climate impact depends on the assumed economic value of all outputs from the process (economic allocation, see Table 28). The highest and lowest values are provided.

7.5.2 DISCUSSION

UNCERTAINTY IN RESULTS

This study concerns an ex-ante LCA of the Spodofos process. An ex-ante LCA uses data based on lab-scale trials, expectations and assumptions, because a process is not yet in operation at the final desired scale. Three more specific observations are important here:

For the Spodofos process, the data used are from lab-scale tests at TRL 5, when processing 10 kg of sludge ash. We recommend performing the analysis again when data from a scaled-up process are available.

The result of the study is largely determined by the climate impact of the avoided products. This assumes that the white phosphorus from Spodofos is a one-to-one substitute for primary white phosphorus, and the same for ground ferrophosphorus (replaces primary ferrosilicon) and ground slag (replaces cement). These primary products were modelled using generic datasets from LCA databases.

ThermusP indicates that there is an uncertainty of about 10% in the electricity and natural gas use of Spodofos. The uncertainty in the inputs of other auxiliaries (excluding aluminium) is about 20%. These uncertainties are included in the analysis, but the margin of error on the overall result is so small that it is not visible in the figures.

CLIMATE IMPACT OF SECONDARY ALUMINIUM

The climate impact of the Spodofos process is mainly caused by the climate impact of the aluminium input. Spodofos uses secondary aluminium from bottom ash. We calculate the climate impact of the secondary aluminium using the Circular Footprint Formula (CFF) from the EU's Product Environmental Footprint methodology. This formula allocates part of the impact of the production of primary aluminium (once needed in an earlier life cycle of the secondary aluminium) to the secondary aluminium.

We only apply the CFF here to the secondary aluminium used as input in the Spodofos process, to make various products. These products are then used and will be discarded at the end of their useful life. If they are recycled at that point, a credit can be allocated for the avoided primary production in accordance with the PEF CFF.

The benefits and climate impact of recycling can also be shared between the recycler and the user of the recycled material(s) in other ways. However, the CFF has the advantage that there is a strong incentive for all parties in the chain to keep and make materials available for subsequent life cycles at the highest possible quality. As such, this is a more conservative and (given developments in LCA methodology in Europe) more robust way of calculating the climate impact of secondary aluminium compared to the earlier Spodofos LCA.

ECONOMIC ALLOCATION

In the analysis from a product perspective, economic allocation is applied to distribute the climate impact of the Spodofos process among the three products. In this LCA it is assumed that the economic value of the intermediate product (e.g. ferrophosphorus before being milled) is equal to the economic value of the final product (e.g. milled ferrophosphorus).

By applying economic allocation, the climate impact of the products depends on the economic value of all three products. If the economic value of one of the products changes (e.g. due to a different application, or changes in the market), this causes a change in the climate impact of all three products. This makes the climate impact of the products from the Spodofos process less certain, as the prices of the products can vary over time.

An alternative to economic allocation is mass allocation. The climate impact of the Spodofos process is allocated among the products based on their mass ratios. Under this form of allocation, most of the climate impact (about 80%) would be allocated to the slag and a much smaller proportion to the phosphorus and ferrophosphorus (both about 10%). The advantage of this form of allocation is that the climate impact of the products does not depend on the application. However, the disadvantage is that mass allocation in this case does not reflect that the goal of the Spodofos process is to recover phosphorus and that ferrophosphorus and slag are by-products.

Given the uncertainty in the economic value of the products, it is recommended to monitor the actual prices of co-products when Spodofos becomes operational. If the prices differ from those assumed here, the product perspective analysis may need to be updated. The analysis from the waste perspective does not involve this uncertainty.

7.6 LITERATURE

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APPENDIX A

INVENTORY FECL$_3$ ROUTE

TABLE 34 DATA INVENTORY OF THE SPODOFOS PROCESS AT THE FECL$_3$ ROUTE, PER TONNE OF SLUDGE ASH

	Unit	Quantity	Comments and modelling *Ecoinvent processes in italics*
Preprocessing sludge ash			
Sludge ash	kg	1,000	Zero climate impact
Electricity	kWh	5.6	Average Dutch electricity mix in 2022 (CE Delft, 2023)
Natural gas	Nm^3	26.4	Production: Natural gas, high pressure {NL}| marketable Combustion: 1.78 kg CO2/Nm^3 (RFO, 2024)
Preprocessing aluminium			
Aluminium	kg	283	20% Aluminium scrap, post-consumer, prepared for melting {RER}| treatment of aluminium scrap, post-consumer, by collecting, sorting, cleaning, 33% Aluminium, primary, ingot {IAI Area, EU27 & EFTA}| marketable See Paragraph 3.2 for explanation
Electricity	kWh	92	See pre-processing sludge ash
RMC-unit and reactor			
Nitrogen	kg	2.2	Nitrogen, atmospheric and 0.21 kWh electricity/kg N for production (Parker Hannifin Corporation, 2013)
Electricity	kWh	31	See pre-processing sludge ash
Product processing			
Electricity	kWh	2.2	See pre-processing sludge ash
Slag processing	kg	1,127	SBK Crushing stony MRPI (NMD 3.9), the climate impact is 0.0015 kg CO$_2$-eq./kg
Diesel oil	ltr	1.4	Diesel, burned in building machine {GLO}| marketable Fuel value: 43.2 MJ/kg (RFO, 2024); Density: 0.84 kg/ltr (Wikipedia, 2021)
Cooling water	ltr	829	Water, cooling, unspecified natural origin, NL
Air and waste treatment			
Electricity	kWh	9	See pre-processing sludge ash
Water	ltr	824	Water, completely softened {RER}| marketable
Caustic soda (35%)	kg	0.5	*Sodium hydroxide, without water, in 50% solution state {RER}| marketable* Correction for concentration
Bleach (12,5%)	kg	1	Sodium hydroxide, without water, in 50% solution state {RER}| marketable Correction for concentration Bleach (12.5% act Cl)
Copper sulphate	g	6.6	Copper sulphate {GLO}| marketable
Dust to landfill	kg	33	Inert waste {RER}| treatment of inert waste, sanitary landfill
Outputs			
Phosphorus	kg	99	
Ferrophosphorus	kg	0	The 119 kg of phosphorus from this process is converted into FeCl$_3$ and calcium phosphate. The calcium phosphate is fed back as input to Spodofos process.
Slag	kg	1,127	

TABLE 35 **DATA INVENTORY OF FERROPHOSPHORUS REPROCESSING TO FECL$_3$, PER TONNE OF FERROPHOSPHORUS**

	Unit	Quantity	Comments and modelling *Ecoinvent processes in italics*
Inputs			
Ferrophosphorus	kg	1,000	
Electricity	kWh	25	Average Dutch electricity mix in 2022 (CE Delft, 2023)
Natural gas	Nm^3	140	Production: Natural gas, high pressure {NL}| market for Combustion: 1.78 kg CO_2/Nm^3 (RFO, 2024)
Slaked lime	kg	580	Sodium hydroxide, without water, in 50% solution state {RER}| marketable
Anhydrous soda	kg	770	Sodium bicarbonate {RER}| marketable
Hydrochloric acid (30%)	kg	5,200	Hydrochloric acid, without water, in 30% solution state {RER}| marketable
Outputs			
$FeCl_3$ (28%)	kg	6,000	
$Ca_3(PO_4)_2$	kg	830	This flow is fed back into the Spodofos process

8

CONCLUSIONS AND FOLLOW-UP

8.1 CONCLUSIONS

From this study and from the findings during the process development in TRL 4 and 5, the general conclusion is that the Spodofos process' unique process flow, its compact design and the negative climate impact provide an extremely good prospect of processing sludge ash into valuable products with a very strong business case. The low climate impact of the products relative to the materials to be replaced makes the process future-proof.

In Spodofos, phosphate is reduced to white phosphorus with aluminium at high temperature. The process shows the following characteristics:
- The conversion of phosphate to phosphorus is complete,
- The phosphorus content in ferrophosphorus is clearly lower than expected,
- A phosphorus recovery efficiency of about 94% is attainable,
- An even higher P yield is possible by post-processing the ferrophosphorus and returning the P product to the input of the process,
- Aluminium costs are lower than phosphorus yields (for sludge ash with average Dutch composition).

Due to its high alumina content, the slag has unique applications with high economic and high sustainability value (such as cement substitute or insulation granulate in refractories). All Spodofos slag from sludge ash can be sold to related industries. The slag contains virtually no heavy metals.

The ferrophosphorus shows the same properties as ferrosilicon, necessary in separation processes (DMS). The prospect of a successful and large-scale application is rated high by an expert. Again, value and sustainability are generated.

The heavy metals accumulating in the ferrophosphorus are immobilised in elemental form due to the strong inert nature of the alloy.

Other heavy metals, except arsenic and cadmium, should be captured in concentrated form from the phosphorus gas stream.

Spodofos' business case was recalculated more accurately with the improved design for the intended plant, and mainly because the product outlets possess considerably more certainty with this study. The projected payback period of less than 4 years at an internal rate of return of 30% is extremely good for a P recovery concept.

By applying new EU guidelines for LCA calculations, the secondary aluminium used in Spodofos is assigned part of the climate impact of primary aluminium. With this, there is no discussion left on the sustainability value of secondary aluminium in Spodofos. The associated CO_2-eq. covers the majority for sludge ash processing. However, all products from Spodofos replace primary products with a very high CO_2-footprint. This compensation means the climate impact is negative, even when including the CO_2-eq. allocated to secondary aluminium. The net CO_2-footprint is calculated at -1.4 tonne/tonne of sludge ash.

After optimisation, the CO_2-eq. allocated to the secondary aluminium may be significantly decreased because the allocation factor is highly price-dependent. Furthermore, the climate impact depends on the sludge ash composition.

However, for a comparison with the climate impact of other P-recycling technologies, hardly no LCAs have been published or otherwise disclosed. Only in STOWA 2023-08 is an LCA of a technology based on acid leaching available. The net climate impact on a product basis of this technology has a positive outcome, potentially higher than the climate impact of its primary replacing product. Recycling therefore further reduces climate impact. Spodofos clearly distinguishes itself in this respect.

Spodofos phosphorus, slag, and ferrophosphorus have a significantly lower climate impact per unit of product compared to the primary products to be replaced: 44%, 75% and 69% respectively.

8.2 FOLLOW-UP

This study suggests that the production of expanded slag and DMS ferrophosphorus is the most certain and shortest route to the realisation of a first Spodofos plant, with all products finding their useful and high-value applications. In the next stages of Spodofos' development, scaling up and controlling the process will be the main objectives. In the pilot, larger quantities of product will be collected. The straightforward approach is to develop the two product applications (cement substitute or insulation granulate and DMS ferrophosphorus) in cooperation with the product partners.

In addition, purification of the phosphorus gas must be developed. The destination of the separated dust and the quality of the phosphorus product can be determined at that point.

During engineering and process layout, efforts will have to be made for slow cooling part of the slag. This may lead to a strong increase in the economic value of slag as granulate in refractory products.

In the next stage of development, a final and practical assessment of the soda-ash leach route is desirable. Although this processing of ferrophosphorus to a coagulant and additional white phosphorus showed difficulties, the sustainability perspective and a circular use of iron in coagulant is attractive. Part of this is the recovery or disposal of copper.

It is very likely that each of the three main products from Spodofos will meet the conditions associated with obtaining end-of-waste status. In subsequent stages of development, the goal is to understand and possibly control the partitioning of heavy metals and their immobility in the slag and ferrophosphorus. The actual acquisition of this status will be applicable at the first full-scale Spodofos plant when producing large quantities. If the end-of-waste status is obtained for all products then Spodofos will no longer be waste treatment.

9

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