THE GRACE PROJECT.
DEVELOPMENT OF OXYGEN CARRIER PARTICLES FOR CHEMICAL-LOOPING COMBUSTION.
DESIGN AND OPERATION OF A 10 kW CHEMICAL-LOOPING COMBUSTOR.

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Abstract

A comprehensive research programme was launched to develop chemical-looping combustion (CLC), a new technology of unmixed combustion with inherent capture of CO\textsubscript{2}, using metal oxide particles for the transfer of oxygen from the combustion air to the fuel.

More than 240 different oxygen-carrier particles produced by extrusion were tested in the initial screening process. Furthermore, more than 50 particles produced by freeze-granulation, and some particles produced by impregnation were also tested. The particles included active oxides of nickel, iron, copper and manganese as well as several different support materials. A limited number of particles were selected for comprehensive testing. Fluidization conditions and recirculation flows were studied in cold-flow models indicating the feasibility of both the full-scale design and a small 10 kW prototype unit.

A 10 kW prototype for chemical-looping combustion was designed, built and run with nickel-based oxygen carrier particles. The prototype uses two interconnected fluidized beds, a fuel reactor where the fuel is oxidized to CO\textsubscript{2} and H\textsubscript{2}O by the oxygen-carrier particles, and an air reactor where oxygen is supplied to regenerate the particles. The air reactor also serves as a riser, providing the circulation of particles between the two reactors. The gases in the two reactors are kept separate by two fluidized particle seals. As far as known this is the first unit where this process has been in continuous operation. Start-up, turn-down and operation of the process were found to be easy. A total operation time of more than 100 h was reached with the same batch of particles, i.e. without adding fresh, unused material. During night-time and during start-up of operation the system was kept at high temperature and in circulation with electrical preheating. Thus, the actual time that the particles have been circulating in the system is close to 300 h.

The fuel used was natural gas, and a fuel conversion efficiency of 99.5\% was accomplished, which is very close to the thermodynamic equilibrium of the NiO/Ni system. It should be pointed out that there is no such thermodynamic restraint for the other metal oxide systems studied. There was no CO\textsubscript{2} in the gas from the air reactor, indicating that a separation efficiency of 100\% is possible. Furthermore, there was no leakage in the opposite direction, i.e. from the air to the fuel reactor, indicating that pure CO\textsubscript{2} can be obtained in the process, except for nickel oxide for which there is a thermodynamic limitation.

Neither decrease in reactivity nor particle strength was seen during the test period. The loss of fines was small and decreased steadily during the test period. In the end of the period the loss of fines, i.e. particles smaller than 45 \( \mu \)m, was 0.0023\% per hour. If this can be assumed to be a relevant measure of the steady-state attrition, it would correspond to a lifetime of the particles of 40 000 h. Assuming a lifetime of 4 000 h, the estimated cost for particles will be low, in the order of 1 \( \text{€/ton CO}_2 \) captured.

A technical evaluation showed that the process uses technology very similar to circulating fluidized-bed combustion. Thus, a chemical-looping boiler can be built with adaptation of well-known technology. A preliminary costing has been performed for a 200 MW\textsubscript{th} chemical-looping combustion boiler for use at BP’s Grangemouth refinery, indicating that CLC should feature strongly among the best options for reducing the cost of CO\textsubscript{2} capture.
Introduction

Chemical-looping combustion

In chemical-looping combustion (CLC) the combustion air and the fuel are never mixed. The system is composed of two reactors, an air and a fuel reactor, see Fig. 1. The fuel needs to be in a gaseous form and is introduced to the fuel reactor, which contains a metal oxide, $\text{Me}_x\text{O}_y$. The fuel and the metal oxide react according to:

$$(2n+m)\text{Me}_x\text{O}_y + C_{n2m} \rightarrow (2n+m)\text{Me}_{x-1}\text{O}_y + m\text{H}_2\text{O} + n\text{CO}_2$$  \hspace{1cm} (1)$$

The exit gas stream from the fuel reactor contains $\text{CO}_2$ and $\text{H}_2\text{O}$, and a stream of $\text{CO}_2$ is obtained when $\text{H}_2\text{O}$ is condensed. The reduced metal oxide, $\text{Me}_{x-1}\text{O}_y$, is transferred to the air reactor where it is oxidized, reaction (2):

$$\text{Me}_{x-1}\text{O}_y + \frac{1}{2}\text{O}_2 \rightarrow \text{Me}_x\text{O}_y$$  \hspace{1cm} (2)$$

The air which oxidizes the metal oxide produces a flue gas containing only $\text{N}_2$ and some unused $\text{O}_2$. Depending upon the metal oxide used, reaction (1) is often endothermic, while reaction (2) is exothermic. The total amount of heat evolved from reaction (1) and (2) is the same as for normal combustion, where the oxygen is in direct contact with the fuel. The advantage of chemical-looping combustion compared to normal combustion is that $\text{CO}_2$ is not diluted with $\text{N}_2$ but obtained in a separate stream without any energy needed for separation.

The reactors in Fig. 1 could be designed in a variety of ways, but two interconnected fluidized beds have an advantage over alternative designs, because the process requires a good contact between gas and solids as well as a significant flow of solid material between the two reactors, [1]. An example of a circulating system composed of two connected fluidized beds, a high velocity riser and a low velocity bubbling fluidized bed, is shown in Fig. 2. The bed material circulating between the two fluidized beds is the oxygen-carrier in the form of metal oxide particles. In the air reactor, or the riser, oxygen is transferred from the combustion air to the oxygen carrier. In the low velocity fluidized bed, or the fuel reactor, oxygen is transferred from the oxygen-carrier to the fuel.

The gas velocity in the riser provides the driving force for the circulation of particles between the two beds. Thus, the particles carried away from the riser are recovered by a cyclone and led to the fuel reactor. From the fuel reactor the particles are returned to the air reactor by means of gravity; the fuel reactor bed is at a higher level than the bed of the air reactor. The gas streams of the two reactor systems are separated by fluidized particle locks. Thus, the system is very similar to circulating fluidized bed combustion of solid fuels, a well established technology which has been used commercially for decades. After condensation of the water, the remaining gas, containing mostly $\text{CO}_2$, is compressed and cooled in stages to yield liquid $\text{CO}_2$. If there is remaining non-condensable gas from this stream containing unreacted combustibles, one option would be to recover this gas and recycle it to the fuel reactor. Small amounts of water left in the liquid $\text{CO}_2$ have to be removed, e.g. by a regenerable solvent, to make the $\text{CO}_2$ flow less corrosive [2]. {insert Fig. 1 & 2 here}

A number of publications related to the development of oxygen-carrier particles have been issued by the research groups at Tokyo Institute of Technology, e.g. [3-4], Chalmers University of Technology, e.g. [5,6], Korea Institute of Energy Research, e.g. [7], TDA Inc, e.g. [8], CSIC-ICB in Zaragoza, e.g. [9], National Institute for Resources and Environment in Japan, [10] and Politecnico di Milano [11]. Also a number of papers investigate the possible thermal efficiencies of power processes involving chemical-looping combustion. However, there seem to be no literature data showing successful operation of a chemical-looping combustor for any longer periods. The only data available is from a small laboratory unit using hydrogen, mixed with 33% argon, as fuel [4]. The system consisted of two interconnected columns, but the principles of the circulation system are not reported and it is not clear if there was any gas mixing between the two reactors. The authors performed tests at 600, 900 and 1200ºC with complete conversion at the two higher temperatures. Gas conversion data are presented for a 5-hour test at 1200ºC. The particles were made of a mixture of NiO and NiAl$_2$O$_4$, and it is interesting to note the high temperature used.

Continuous testing in a chemical-looping prototype was not only needed to demonstrate the principle of this new combustion technology and thus give credibility to a technology that had never previously been tested in practice. It was also essential to verify the usefulness of the particles developed. Most laboratory tests of particle reactivity
cover only a limited number of cycles. Furthermore the laboratory tests do not show if the particles would be degraded by attrition or fragmentation at the velocities in a full-scale unit.

Objectives and organization

The objective of the project was to develop a new combustion technology - chemical-looping combustion - with inherent capture of the greenhouse gas carbon dioxide. The intended application is the Grangemouth refinery, where 4.2 million tons of CO$_2$ is emitted yearly, of which half is to be captured and stored in the Forties oilfield. The resulting technology could be an option for all applications where gaseous fuels are used in units of sufficient size for a cost-effective handling and transportation of the CO$_2$ captured. The ultimate goal is a combustion process with no emissions, high efficiency and low costs. The project was organized to produce the knowledge needed to promote development of this process, including:

- Development of oxygen-carrier particles of sufficient reactivity and life-time.
- Study of reactor system in order to establish possible conditions for fluidization and solids recirculation.
- Demonstration and evaluation of this new combustion technology in a prototype unit, including verification of the performance of the particles developed.
- Assessment of the feasibility of a full-scale plant and prediction of capital and operating cost.

The partners in the GRACE project were CSIC in Zaragoza, leading the development of oxygen carrier particles, Technical University of Vienna, working with the reactor system and fluidization conditions, Chalmers University of Technology, involved in the development, construction and operation of the demonstration unit and to a lesser extent in the particle development, Alstom Power Boilers, assessing the feasibility of the full-scale plant and the doing costing, and BP, acting as coordinator and providing the settings for the full-scale plant.

Experimental

Development of oxygen-carrier particles

Particles were produced primarily by two methods, extrusion and freeze-granulation, and the reactivity was also assessed by two methods, thermogravimetric analysis as well as tests in small fluidized-bed reactors with analysis of exiting gases. In the reactivity tests the particles are subject to alternating oxidizing and reducing conditions, simulating the cycles the particles will experience in a real system when they are circulating between the fuel and the air reactor. Furthermore the crushing strength of the particles was measured. The main criteria used in the evaluation are reactivity, crushing strength, and low tendency of agglomeration.

Study of reactor system

The study of reactor systems was made using cold-flow models of perspex glass, and three such models were studied in detail:
- A model of the 10 kW prototype to be built within the project
- An alternative model for a 10 kW prototype with advanced options for recirculation
- A large-scale reactor concept simulating a 0.5 MW boiler, this unit was also designed so that it would give relevant information for the 200 MW boiler proposed by Alstom Power Boilers in this project.

Design of a 10 kW chemical-looping combustion (CLC) prototype

The 10 kW prototype was not designed primarily to be a small model of a full-scale unit, but to obtain a unit that works, is flexible and can be used to study particles and reactions in continuous operation. Natural gas with 88% methane (CH$_4$) and a H/C ratio of 3.7 was used as fuel and tests were made at ambient pressure with a nickel-based and an iron-based oxygen carrier.
Results and Discussion

Development of oxygen-carrier particles

In the first phase of the project 240 particles were produced by extrusion and tested by thermogravimetric analysis. The test matrix included four active metal oxides (Cu, Fe, Mn and Ni), five inert materials acting as support (Al₂O₃, sepiolite, SiO₂, TiO₂ and ZrO₂), four sintering temperatures (950, 1100, 1200 and 1300°C) and three mass fractions of active metal oxides (40, 60 and 80%, with the balance being the inert material). A number of particles could be discarded because of softness, melting, or low reactivity and from the remaining particles the most promising combinations of active oxides and support materials were found to be SiO₂ or TiO₂ for Cu, Al₂O₃ and ZrO₂ for Fe, ZrO₂ for Mn and TiO₂ for Ni. A selection of interesting particles was then produced by freeze-granulation and tested in a laboratory fluidized bed. Some deviations from the basic test matrix were tested in order to see if particles could be improved further, the main reason for this being that many of the most reactive freeze-granulated particles were found to be too soft. In total 56 freeze-granulated particles were tested. The extruded particles were cylindrical with a diameter of approximately 2 mm. The freeze-granulated particles were spherical and a size fraction of 125-180 μm was used in the laboratory tests. In addition a number of particles were made by impregnation of porous particles with an aqueous solution of Cu(NO₃)₂.

Selected particles were investigated in more detail, including extended tests with 100 cycles, attrition tests in a small fluidized bed, studies of the effects of temperature and gas concentrations as well as determination of kinetic parameters. Eventually the testing resulted in three particles, and from these one nickel-based and one iron-based were selected to be produced in large quantities for the prototype testing. More detailed results from the particle development can be found in existing and future publications, e.g. [5,9,13-14].

Study of reactor system

In cold-flow models it is possible to vary operating conditions over a wide range and study the effect on the system pressure balance, the solids circulation rate, the particle residence time distribution, and the gas leakage between the air and the fuel reactor. Thus, these models provide an important tool to support the design of CLC systems.

The cold-flow model of the 10 kW prototype was built with the principal design shown in Fig. 2, the major difference being in the geometry of the reactors. Firstly, the fuel reactor is conical to accommodate for the gas volume expansion because of reaction, e.g. CH₄ to 2H₂O and CO₂. Secondly, the air reactor has a wider bottom section and a thinner riser, in order to achieve a stable bottom bed, to reduce the heat losses of the upper part and to reach the high gas velocities of full-scale units. The latter is relevant for evaluation of the attrition of tested particles. The tests in the cold-flow model of the 10 kW prototype verified the flexibility of the design and only minor modifications were made for the hot unit, [12,15]. The tests in the cold-flow model corresponding to the 0.5 MW demonstration unit indicated the feasibility of this design, and also provided a basis for the 200 MW boiler design, [15].

Overview of operation in chemical-looping mode

A total of more than 100 hours of operation of the 10 kW chemical-looping combustor prototype with nickel-based particles was accomplished with the same batch of particles, i.e. without adding fresh, unused material, [16]. During the nights the fuel was switched off and the unit was operated with electrical preheating, and this was continued until operation was resumed on the following day. Thus, in addition to the actual CLC operation, the particles have been in circulation at high temperature without fuel addition. Therefore the total time of circulation of the particles is almost 300 h.

Almost full conversion of the fuel, natural gas, was accomplished. No CO₂ was found in the gas from the air reactor. Operation was very stable, i.e. the process could often be run until the fuel addition was stopped for the night without any modifications of the operation, such as adjustments of gas flows. A number of technical problems, such as gas and particle leakages, failures of data acquisition etc. were encountered during operation.
There were, however, no real difficulties related to the actual process and only two minor things had to be addressed:

i) In the first hours of operation of the first day, the gas velocity in the particle locks was insufficient, resulting in particle circulation failure. After adjusting the gas flow, circulation was restored.

ii) After an extended time of operation the elutriation of particles resulted in poorer circulation because the smaller particles are preferentially elutriated, which results in coarser particles in the system. Thus, the flow/velocity in the air reactor had to be increased to achieve sufficient circulation, i.e. sufficient temperature in the fuel reactor. After some days of operation elutriated particles were added back to the system. Thus, elutriated particles were recycled twice during the test period, i.e. on day six and day ten of the twelve days of operation.

Gas concentrations and temperature dependence

The measured concentration is close to equilibrium for carbon monoxide (CO) if dilution is considered, see Fig. 3. In the prototype tests there is a dilution of the gas with the inert gas used to fluidize the particle locks, typically the concentration is reduced by 20-30% depending on the flows. In a full-scale system steam would be used as fluidization gas in the particle locks, thus avoiding any dilution of the CO₂ produced. Hydrogen (H₂) was not measured on line, but bag samples showed that the H₂ concentration was 1%, which is very close to thermodynamic equilibrium if dilution with inert gas is considered. {insert Fig. 3 here, (or below together with Fig 4.)}

The measured concentration of methane in the gas from the fuel reactor varied between 0.05 and 1% in the temperature range 800-900°C. The higher values were, quite unexpectedly, seen for higher temperatures in the fuel reactor, Fig. 3. The equilibrium concentration of methane is below 10⁻⁶ ppm in this temperature range, i.e. zero for all practical purposes. Furthermore, it would be expected that higher temperatures would increase the reaction rates and thus improve the conversion. However, the temperature dependence of methane seems to be an artifact caused by the correlation between the temperature in the fuel reactor and the mass flow of recirculating particles.

It is known from the laboratory testing that Ni-based oxygen carriers during reduction show an initial peak of methane of approximately 1%. This peak disappears as the conversion of the NiO to Ni proceeds. No similar peak has been seen for other metal oxides. Ni is a known catalyst for the reaction between CH₄ and H₂O and it is believed that this behaviour is a result of the beneficial catalytic effect of the reaction product, promoting intermediary reactions. In other words, an increased circulation reduces the presence of Ni so much that methane conversion is decreased.

In a small unit such as the 10 kW prototype, the relative heat losses from the fuel reactor are larger than in a full-scale unit, resulting in the need for a higher recirculation. Thus, lower circulation should be possible without loss in temperature in a full-scale unit, which is expected to improve the methane conversion. Clearly this needs further investigation.

No CO₂ could be found in the gas from the air reactor, indicating that there was no significant gas leakage from the fuel to the air reactor. This also shows that no char was formed in the fuel reactor that was transferred to the air reactor with the particles. The leakage from the air to the fuel reactor was studied by measuring the oxygen concentration in the off-gas while adding nitrogen to the particle locks and the fuel reactor. The gas leakage was below the detection limit with the analysers used, i.e. the dilution of the gas from the fuel reactor is less than 0.5%.

Loss of fines

Attrition or fragmentation of particles leading to the production of fines is critical for the lifetime of the particles. It is therefore essential to analyse the production of fines. The loss of fines is here defined as the loss of particles smaller than 45 μm. It is assumed that particles below this size will have a short residence time in a commercial unit and thus be of little use in the process, whereas it would be meaningful to recycle larger particles. In Fig. 4 shows the loss of fines versus time. The loss of fines includes particles elutriated from the air reactor, i.e. captured in a filter, and from the fuel reactor, i.e. captured in a water trap. For practical reasons the particles in the water trap were not collected daily, which explains the plateaus in this curve. It is clear that the loss of fines is rapidly decreasing with time during the whole test period. Two mechanisms can explain this decrease, that is i) fines present
with starting material and ii) a gradual decrease in the attrition of particles, for instance because the material becomes harder or because irregularities are gradually worn off. {insert Fig. 4 here}

The latter is supported by photos of the particles, see Figs. 5 and 6. It can be seen that smaller spheres, “satellites”, are sintered onto the larger spheres or together in groups. It is likely that an important mechanism for production of fines is associated with these “satellites” being ripped from the larger particles. It is also clear from photos of particles elutriated later during the test series that the number of satellites has decreased, although satellites still remain after 100 h of operation [16]. {insert Figs 5 and 6 here}

After day three, when most of the fine material added with the original particles has been elutriated, there is a slower but seemingly exponential decrease in the particle loss. In this period the loss of fines is reduced to half every three days.

The loss of fines in the size fraction below 45 μm is 0.0023%/hour at the end of the period, see Fig. 4. If this value can be taken as a measure of the lifetime of the particles, this leads to an approximate lifetime of the particles of 40 000 h. This indicates that the lifetime of these particles may be very long, provided that there is no chemical degradation. This would of course have to be verified by testing for longer periods.

An important question regarding the data on particle loss is the relevance of those data for large units. Attrition is related to the velocity in the riser and the velocity of the gas coming out of the air distributor nozzles in the bottom bed. The fluidization velocity in the prototype air reactor was considerably lower than expected for a large unit. However, because of the area decrease into the riser, the riser velocities during operation are typical of a full-scale unit. Furthermore the velocities from the inlet nozzles were very high during night operation without reaction, i.e. with preheating, in the order of 100 m/s. This velocity is much higher than that expected from nozzles in a full-scale plant, and may be an important source for attrition during the tests in the prototype. It is therefore believed that the tests in the prototype do not underpredict the attrition in a full-scale unit.

Tests of the oxygen-carrier particles in the laboratory after the 100 h of operation indicate that there was no loss in reactivity or any decrease in the crushing strength of the particles.

Cost of NiO-based particles

With nickel being the most expensive of the raw materials used, the cost of raw material is assumed to be 3 €/kg. The cost of manufacture by spray-drying, sintering etc. is estimated to 1 €/kg, considering a loss in sieving because of demands for a limited size range. This gives a total cost of 4 €/kg. If fine material lost from operation can be recycled this would reduce the cost significantly, but not below the production cost.

The solids inventory in the prototype differs much from what is expected in a large unit. Firstly, the bed height of the fuel reactor was dimensioned for less reactive iron-based oxygen-carriers, and secondly the bed of the air reactor is much larger to achieve stable conditions in this small unit. Therefore, as far as solids inventory is concerned, no certain conclusions can be drawn from the tests. Based on the laboratory tests, it is assumed that the solids inventory in a full-scale unit is in the order of 100-200 kg/MW.

The total cost of particles per ton of CO$_2$ captured is determined by three assumptions, particle inventory, lifetime and specific particle cost. Table 1 summarizes the estimation of the particle cost. The numbers used for all three of the assumptions are conservative, see notes in the table. There has previously been a concern that the cost of the particles could be a show-stopper for this technology. With an estimated cost of the particles of the order of one €/ton of CO$_2$ captured, this should not be the case. {insert Table 1 here}

Feasibility of 200 MW plant and prediction of capital and operating cost

Circulating fluidized-bed combustion (CFBC) of solid fuels is a well established commercial technology, with boilers of sizes up to 600 MWe designed and 250 MWe already in operation. Chemical-looping combustion of refinery fuel gas involves technology well known because of the similarities to CFBC: i) the air reactor is equivalent to the combustor, ii) the cyclones have similar duties, except that the flow-rates are somewhat higher in
the chemical-looping combustion, iii) the backpass has similar duties, iv) the external fluidized-bed heat exchanger (FBHE) has similar duties and v) the fuel reactor will be connected similarly as the FBHE and will be similar to smaller fluidized-bed boiler systems, except that it is adiabatic. Consequently, the costing of such a system can be based on components from well-known commercial technology, [17].

A preliminary costing has been performed for a 200 MWth chemical-looping combustion circulating fluidized-bed (CLC CFB) boiler for use at BP’s Grangemouth refinery. Preliminary indications from CCP (CO2 Capture Project) economic assessments suggest that CLC should feature strongly among the best options for reducing the cost of CO2 capture, [17]. It appears that there are no insurmountable issues for the technology, which reuses mostly existing CFBC know-how. The oxygen-carrier is the main uncertainty in terms of cost and durability.

The longer term development of the supercritical steam cycle adaptation to chemical-looping combustion using CFBC technology appears as a real possibility and a limited challenge.

Conclusions

A comprehensive research programme was undertaken to develop chemical-looping combustion technology. Firstly, a large number of possible oxygen-carrier materials were produced and tested with the best ones selected for further testing and development. Secondly, fluidization conditions and recirculation flows were studied in cold-flow models indicating the feasibility of both the full-scale design and a small 10 kW prototype unit. Thirdly, a 10 kW prototype unit was constructed and operated, demonstrating both this new combustion process as well as the durability of the oxygen-carrier particles under realistic process conditions. Lastly, a preliminary costing of a 200 MWth chemical-looping boiler unit for refinery gas combustion has been performed, indicating that CLC should feature strongly among the best options for reducing the cost of CO2 capture.

Some important results obtained in the prototype testing are:
- A total operation time of more than 100 h was reached with the same batch of particles, i.e. without adding fresh, unused material. Including night-time and start-up, when the system was kept circulating at high temperature with electrical preheating, the actual time that the particles have been circulating in the system is close to 300 h.
- A high conversion of the fuel was accomplished, with approximately 0.5% CO, 1% H2 and 0.1% methane in the exit stream, which is very close to thermodynamic equilibrium. The presence of these compounds corresponds to a fuel conversion efficiency of 99.5% based on fuel heating value.
- There was no detectable gas leakage between the two reactors. Firstly, no CO2 escapes from the system via the air reactor. Thus, 100% of the CO2 is captured in the process. Secondly, the leakage of gas from the air reactor to the fuel reactor was below the detection limit. Thus, the CO2 leaving the fuel reactor should be pure, with the exception of any unconverted fuel, or inert compounds associated with the fuel, e.g. N2.
- No decrease in reactivity was seen during the test period. This was also verified by laboratory analyses of particles elutriated from the system at the end of the testing period. Furthermore, analyses of crushing strength indicated that the particles after 100 h of operation still were as hard as the original particles.
- The loss of fines was small and decreased continuously during the test period. In the end of the period the loss of fines, i.e. particles smaller than 45 μm was 0.0023% per hour. If this is assumed to be a relevant measure of the steady-state attrition, it corresponds to a lifetime of the particles of 40 000 h. Assuming a lifetime of the particles one order of magnitude lower, i.e. 4000 h, the cost of particles in the process is estimated to be below 1 €/ton of CO2 captured.

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References


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<th>Table 1. Particle costs</th>
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<td>particle inventory¹</td>
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<td>lifetime²</td>
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<td>specific emission</td>
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<td>resulting particle cost</td>
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¹ Somewhat uncertain value, but without doubt in the correct order of magnitude.
² Loss of fine material in prototype tests suggests a lifetime that is 10 times longer, i.e. 40 000 h.
³ If fine material lost in the process can be used as raw material in the production, the costs can be decreased significantly, but not below the production cost of approximately 1 €/ton.
Fig. 1. Chemical-looping combustion. MeO/Me denote recirculated oxygen carrier solid material.

Fig. 2. Layout of chemical-looping combustion process, with two interconnected fluidized beds. 1) air reactor, 2) cyclone, 3) fuel reactor.

Fig. 3. CO (continuous line) and CH\(_4\) (\(\times\)) versus fuel reactor temperature.

Fig. 4. Fractional loss of fines vs. time. Time of recirculation includes period with no reaction.

Fig. 5. Photo of material added to the prototype.

Fig. 6. SEM photo of particles in Fig. 5.