



# Energy savings in the production chains of Tronox - Public -

## **Report**

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# Summary

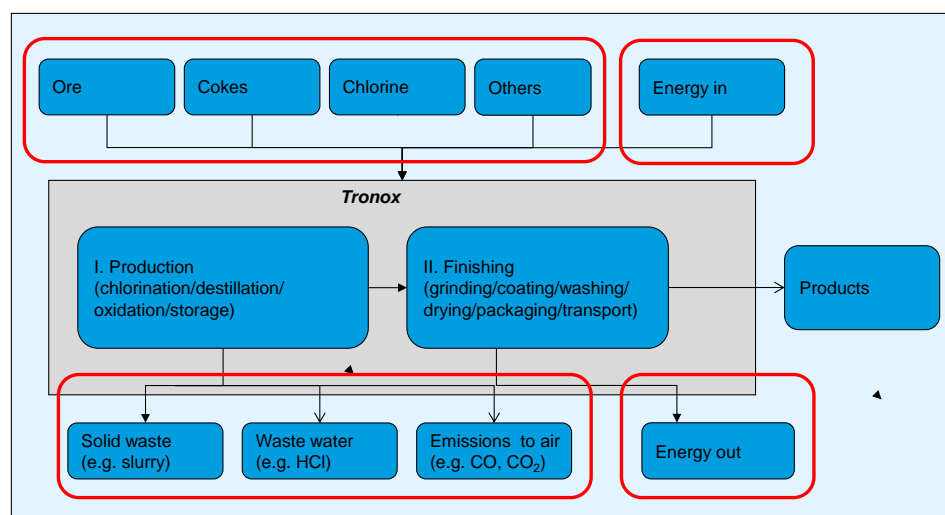
Tronox works continuously on improving energy efficiency of its operations, both within its site and together with neighbours at the Botlek chemical site.

As a participant in the Dutch MJA3, a long term agreement on energy efficiency, Tronox also wants to look at options for improving energy efficiency in the wider product chain. In this context, a study was undertaken on measures for increasing energy efficiency outside the scope of process efficiency.

This study has been financed and commissioned by NL Agency in the context of the Long-Term Agreements (LTAs) on energy efficiency in the Netherlands. These agreements have been made between the Dutch Ministry of Economic Affairs, Agriculture and Innovation (EL&I) and industrial sectors, and aim at promoting energy savings. Target is to substantially reduce the required energy per unit product. The LTA programme is implemented by NL Agency, a department of the Ministry of EL&I ([www.agentschapnl.nl/mja](http://www.agentschapnl.nl/mja)).

The study focussed on potential measures in the supply of raw materials, the use and discharge of energy and the waste streams (solid waste streams, as well as emissions to air and water). Focus areas are indicated in Figure 1.

Figure 1 Main raw materials, products and side streams of Tronox' production process



Following a brainstorm and discussion, a number of possibly attractive and realistic measures were identified. The following ideas were investigated further:

1. Purify HCl and sell as product.
2. Use of waste heat for city district heating.
3. Separate and sell CO<sub>2</sub> and CO as products:
  - a CO<sub>2</sub> to greenhouses.
  - b CO to industrial clients.
4. Use of calcinated biocokes as petrocokes substitute.
5. Use of slurry waste stream as secondary construction material.

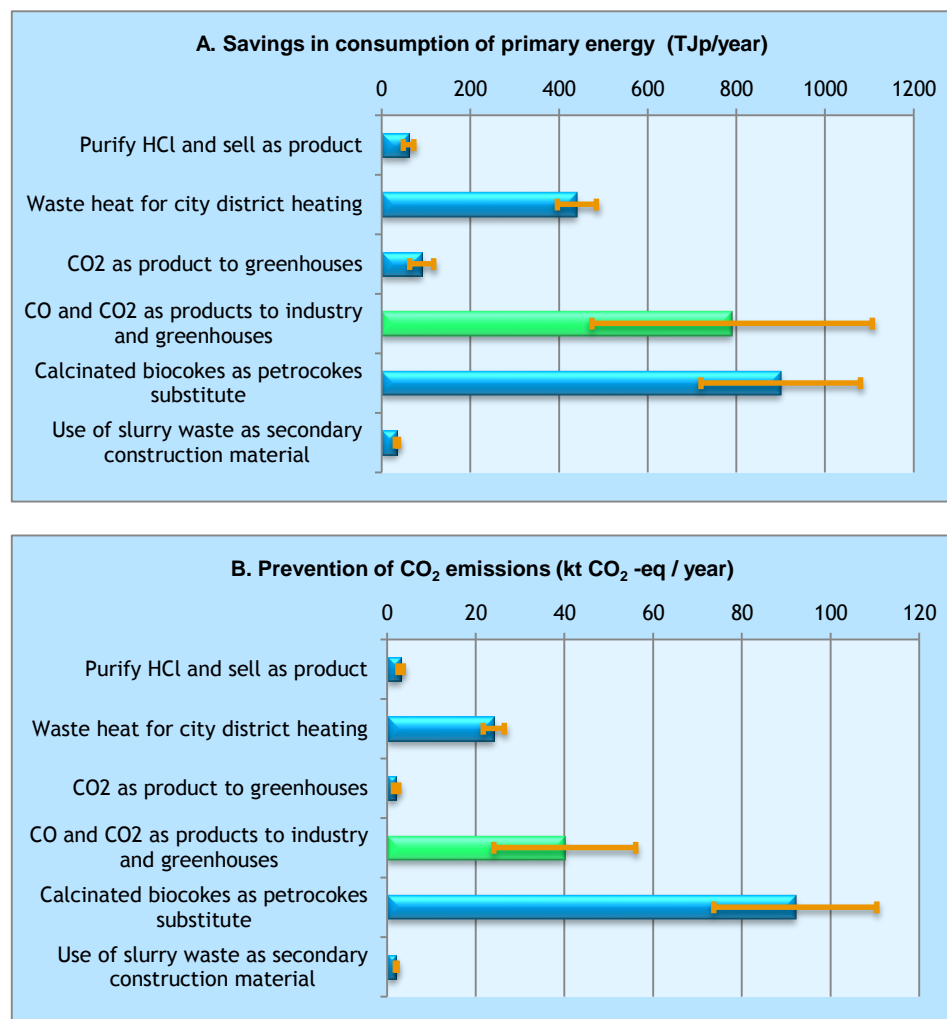
In this report, for these possible measures the potential effects on energy efficiency and CO<sub>2</sub> savings are quantified. Where applicable, a judgement on feasibility (technical/economical) is also given.

Results for energy savings and CO<sub>2</sub> emission reductions are shown in Figure 2.

The five measures have a combined energy savings potential of approximately 1.5 peta joule (1.5 mln GJ). The potential for prevention of CO<sub>2</sub> emissions would be about 120 kt CO<sub>2</sub> eq. per year. The figures have been derived from data that has uncertainties, the combined uncertainty is about  $\pm 25\%$ .

The measures do also have a substantial impact on the GHG emissions in the production chain. Compared to a typical value of 6 kg CO<sub>2</sub> eq./kg TiO<sub>2</sub>, the options might contribute to a saving of 25% in the production chain.

**Figure 2** Effects of measures identified on savings in consumption of primary energy (a) and emissions of CO<sub>2</sub> (b). Overall the measures amount to an energy saving potential of 1.5 PJp and 120 kton CO<sub>2</sub> emission reductions<sup>1</sup>



<sup>1</sup> The 3<sup>rd</sup> (sale of CO<sub>2</sub> to greenhouses) and 4<sup>th</sup> options are alternatives, the overall potential is calculated with Option #3.



The savings potential is a technical potential. Actual possible implementation of the measures will depend on a more detailed examination on the economics of the different measures, which is the logical next step to be undertaken.

A 1<sup>st</sup> assessment of the technical and economical feasibility is given in Table 1. Apart from the option of separation CO and/or CO<sub>2</sub>, the options could be considered interesting.

Table 1 Evaluation of measures

	Technical feasible	Economical feasible	Environmental impact	Potential action of Tronox
Purify HCl and sell as product	Yes	Potentially	Limited	Contact with HCl producers merchants
Use of waste heat for city district heating	Probably	Potentially	Large	Feasibility study
Separate and sell CO <sub>2</sub> and CO as products: CO <sub>2</sub> to greenhouse farmers	Probably	Probably not	Large	None
Use of calcinated biocokes as petrocokes substitute	Not yet proven	Potentially	Very large	Contribution in feasibility study with Norit and Eneco (if facilitated by national government)
Use of slurry waste stream as secondary construction material	Yes	Yes	Limited	Green Deal







# 1 Introduction

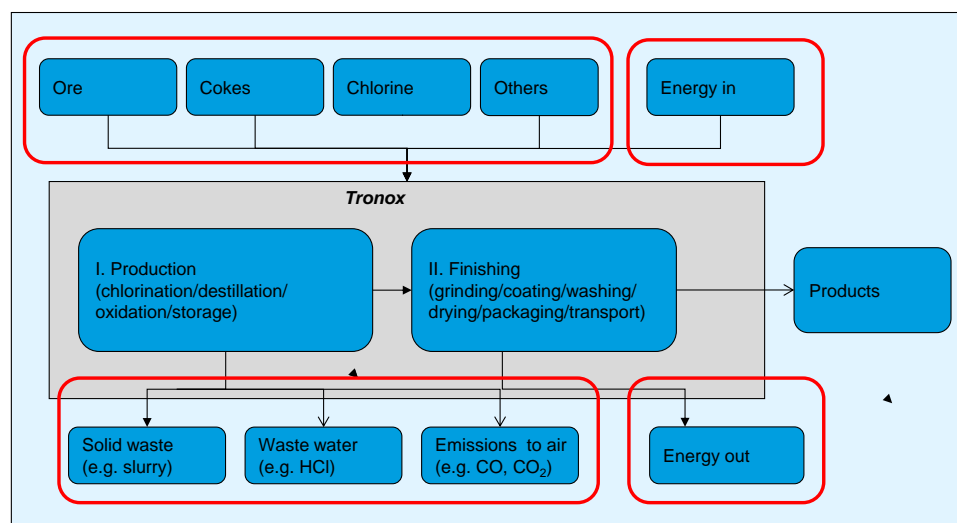
On a day-to-day basis, Tronox works on improving the energy efficiency of its operations. The target in the MJA-3 covenant is to reach for a 30% improvement of production energy efficiency in the period 2005-2020. Part of this will be realised by improved process efficiency, and part of it by options that go beyond the production site. Also by studying options for energy efficiency gains within the wider production chain and by possible interactions with parties outside of the direct production chain, the so called 'chain measures', savings and therefore efficiency gains can be achieved. This investigation is directed at identifying options for energy savings in the production chains of Tronox.

This study has been financed and commissioned by NL Agency in the context of the Long-Term Agreements (LTAs) on energy efficiency in the Netherlands. These agreements have been made between the Dutch Ministry of Economic Affairs, Agriculture and Innovation (EL&I) and industrial sectors and aim at promoting energy savings. Target is to substantially reduce the required energy per unit product. The LTA programme is implemented by NL Agency, a department of the Ministry of EL&I ([www.agentschapnl.nl/mja](http://www.agentschapnl.nl/mja)).

## Scope

The investigation focusses on energy savings in the use of raw materials, reuse of rest materials in waste streams (solid waste streams as well as emissions to air and water), and the use of waste streams of energy. This is illustrated in Figure 3.

Figure 3 Scope of study. The project focusses on options for energy savings in the use of raw material, waste streams and supply and discharge of energy streams



Following a brainstorm and discussion, a number of possibly attractive and realistic energy efficiency 'chain' measures were identified. The most attractive are:

1. Purify HCl and sell as product.
2. Use of waste heat for city district heating.
3. Separate and sell CO<sub>2</sub> and CO as products:
  - 3a. CO<sub>2</sub> to greenhouses.
  - 3b. CO to industry.
4. Use of calcinated biocokes as petrocokes substitute.
5. Use of slurry waste stream as secondary construction material.

### Methodology

Energy savings are expressed in *primary energy*. This means that e.g. electricity savings are expressed in savings of the energy values of the primary fuels used in electricity production. The unit is tera joules of primary energy per year (TJp). Where applicable, use is made of figures from Agentschap NL, such as GER values<sup>2</sup>.

In quantifying *greenhouse gas emission reductions*, we have calculated with emission factors from Agentschap NL.<sup>3</sup>

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<sup>2</sup> Agentschap NL, 2012a: GER-waarden database (MJA)  
<http://www.agentschapnl.nl/content/ger-waarden-database-mja>.

<sup>3</sup> Agentschap NL, 2011: Nederlandse lijst van energiedragers en standaard CO<sub>2</sub>-emissiefactoren (update 2011). [http://www.broeikasgassen.nl/docs/Vreuls 2011 \(NL\) Ned brandstoffenlijst januari 2011.pdf](http://www.broeikasgassen.nl/docs/Vreuls%202011%20(NL)%20Ned%20brandstoffenlijst%20januari%202011.pdf).



## 2 Measure ‘Purify HCl and sell as product’

### 2.1 Main findings

If the total side stream of HCl produced could be reused this would imply a gross saving in fossil energy use of 60 TJ/year, and a reduction of greenhouse gas emissions of 3 ktonnes CO<sub>2</sub> eq./year. If only the side stream from the gas cleaning is reused, this will maximally save 38 TJ/year and allow a reduction of 1.9 ktonnes CO<sub>2</sub> eq./year.

Investigating the technologies for reprocessing of contaminated hydrochloric acid solutions into a sellable quality we reached the following conclusions:

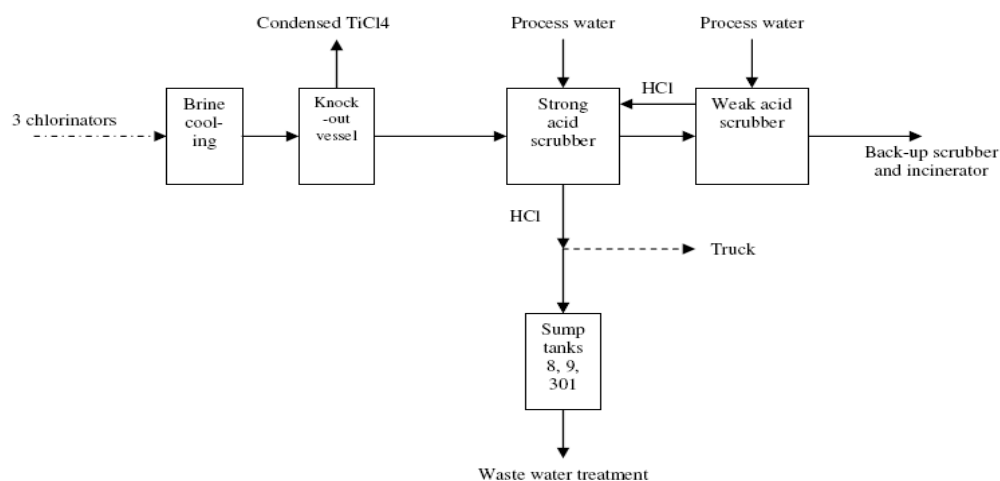
- HCl rectification technologies do not offer additional benefit compared with coagulation technology, which was previously analysed by Tronox;
- several merchants and producers have been contacted. Some of them appear to be interested;
- no technology to produce CaCl<sub>2</sub>-solution is readily available.

### 2.2 Motivation to investigate purification measures

#### 2.2.1 Side stream under consideration

The gas cleaner of Tronox produces hydrochloric acid containing side streams. This side stream is produced in the scrubbers where most of the hydrochloric acid is removed in either the ‘strong acid’ or the ‘weak acid’ scrubber, see Figure 4.

Figure 4 PFD acid scrubbers Tronox



Source: Tronox.

There is a market for concentrated hydrochloric acid solutions. However, in the current situation the hydrochloric acid solution as produced by the scrubbers has no useful application, such as mordant in the metal industry,



mainly due to the elevated concentrations of some metals. Therefore this solution is currently neutralized with lime milk and discharged as waste water.

Reuse of the hydrochloric acid solution as produced by the scrubbers would save the cost for lime.

### 2.2.2 Environmental benefits of reuse

If reuse leads to the reduction of primary production of hydrochloric acid, then it creates a decrease in the consumption of fossil fuels and the related greenhouse gas emissions. In this study we assume that reuse of hydrochloric acid produced by Tronox causes the ousting of the primary production of hydrochloric acid from hydrogen and chlorine<sup>4</sup>.

Per ton of pure HCl the production of primary acid requires primary energy and causes greenhouse gas emissions (Ecoinvent, 2006). Reuse of the HCl sidestream of Tronox would result in a gross savings in fossil energy consumption of 0.038 PJ/year and would yield a reduction of greenhouse gas emissions of 1.9 kilotons CO<sub>2</sub> eq./year.

## 2.3 Processes considered to allow for reuse

This study considers four options for reusing the hydrochloric acid solution produced by the scrubbers. The first option is purification of the waste water stream with a coagulant, via the Kemira Savannah technology. This option was previously evaluated by Tronox. This route appears technically feasible, but it has not yet been possible to create a commercially attractive business case with a party on the HCl-market. This process is used as a reference case in this study. In consultation with Agentschap NL and Tronox, three other processes were selected for further consideration:

- the production of a calcium chloride (CaCl<sub>2</sub>) solution that could be sold as road salt;
- reprocessing of the hydrochloric acid to a sellable concentrated solution (30% HCl);
- transport of the waste water stream of Tronox to German waste incineration plants; production of hydrochloric acid in these plants.

### 2.3.1 Purification of waste water stream with a coagulant (Kemira Savannah technology)

This process was evaluated before by Tronox. This process purifies the hydrochloric acid solution by adding a coagulant, after which the gel containing the contaminations can be removed by means of filtration.

In 2009 this technology was deemed technical feasible, but lacked economical viability. The main costs were related to the required investments, operational costs and transport costs. The main benefits were the saving on the use of lime.

### 2.3.2 CaCl<sub>2</sub> production

The Energy Company of the Amsterdam municipality (AEB) developed and patented a technology for production of a pure CaCl<sub>2</sub> solution. The technology was designed to reprocess hydrochloric acid solutions produced by waste incineration in AEB's waste incineration plants (WIPs).

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<sup>4</sup> However, it should be noted that hydrochloric acid is mainly produced as a by-product of for example the PVC production chain (Ecoinvent, 2006). Ousting of such products is unlikely, since the price of the by-products has no significant influence on the amount of main product produced.



In practice, the technology still has a few teething problems to solve. Currently the costs for further development of the technology and the product certification of the  $\text{CaCl}_2$  solution under REACH pose insurmountable obstacles. Therefore a weaker  $\text{CaCl}_2$  solution is produced, which is discharged into the North Sea. This technology is not further analysed.

### 2.3.3 Production of a concentrated hydrochloric acid solution (30% HCl)

The second alternative technology: distillation, purification and evaporation of hydrochloric acid solution - is based on a technology used by six Waste Incineration Plants in Germany.

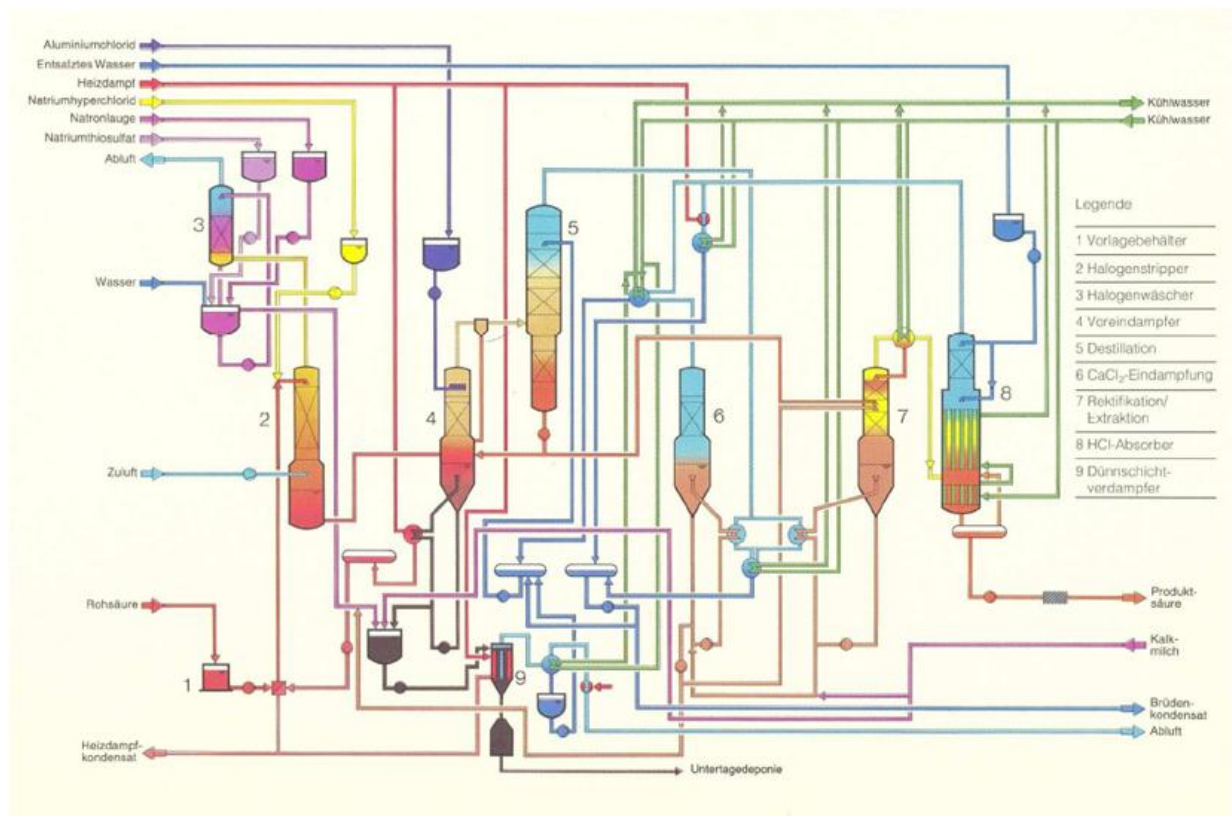
In these six plants, a 30% solution of concentrated HCl is produced on the basis of the heavily contaminated hydrochloric acid solution of the flue gas cleaning of these waste incineration plants. The product is sold to the metal industry, where it is applied as a mordant. A process diagram is shown in Figure 5.

Most steps in this technology are not relevant to the situation at Tronox:

- Tronox can already produce a highly concentrated solution, so evaporation and distillation are not necessary;
- in the raw acid produced by Tronox there are no other halogens present, so stripping for removal of these substances is not necessary.

In short this process seems to provide a too extensive pretreatment of the considered HCl solution.

Figure 5 Process-scheme of the HCl rectification installation



#### **2.3.4 Transport of HCl-waste stream to incinerators; production of HCl in incinerators**

An alternative idea is transport of Tronox' HCl-waste to incinerators in Germany, adding it to the HCl stream of these plants, for production of HCl. This option appears not realistic since the volumes of HCl produced by the AVIs are substantially (a factor 3) smaller than the volumes produced at Tronox.

### **2.4 Sale of HCl stream from gas cleaning**

Since the processes described above all came at too high costs, we investigated the possibilities for direct sale of the HCl stream by contacting merchants and producers of industrial HCl.

#### **2.4.1 Market for industrial HCl**

Major producers worldwide include Dow Chemical at 2 million metric tons annually (calculated as HCl gas), Georgia Gulf Corporation, Tosoh Corporation, Akzo Nobel, and Tessenderlo at 0.5 to 1.5 Mt/year each. Total world production, for comparison purposes expressed as HCl, is estimated at 20 Mt/year, with 3 Mt/year from direct synthesis, and the rest as secondary product from organic and similar syntheses. By far, most hydrochloric acid is consumed captively by the producer. The open world market size is estimated at 5 Mt/year (IHS, 2012).

#### **2.4.2 Market developments in EU**

The supply of industrial HCl is high, which keeps the prices relatively low (currently the SGA price for clean 30% HCl is 35-40 €/tonne).

Prices on the European markets are expected to decrease since BASF announced the construction of a new TDI plant increasing the net production of TDI with 220,000 tonne/year, starting in 2014 (BASF, 2012), while Bayer announced the construction of a multipurpose production plant for hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) starting from 2013 (Bayer, 2012). Together these plans imply an additional production of about 1,000,000 ton/year of 30% HCl, in the EU Market.

#### **2.4.3 Market developments in the USA**

The demand for industrial HCl is high, mainly due to additional demand related to shale gas extraction. However, for this application there is a strong preference for 33% HCl, and there is a strong competition from HCl from India.



# 3 Measure ‘Use of waste heat for city district heating’

## 3.1 Main findings

Using 18 MW of at Tronox available waste heat for city heating will result in large energy savings of up to 440 TJ/y and of 24 kt of CO<sub>2</sub> emissions prevented per year. This incorporates energy losses in the transmission system and in the district heating system.

This is an upper limit estimate, actual savings depend on what fraction of the amount of heat available at Tronox is delivered to the heat transport system and the city. Not assessed are the economics and technological aspects required to overcome the low pressure and air content of the steam available.

## 3.2 Available heat

Tronox has a surplus of waste heat (steam) at 200 °C available: 18 MW, originating from the steam mills. The steam is at approximately atmospheric pressure, making it significantly superheated. In addition, the steam contains a fraction of air.

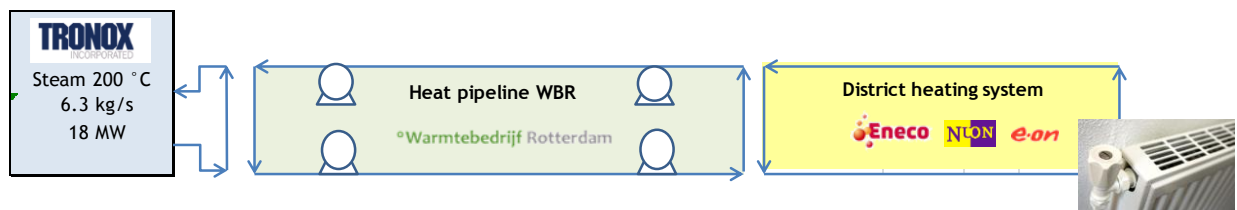
These characteristics make heat transfer difficult. Either large heat exchanger surfaces will be required, or the steam has to be worked up to a level closer to the saturation point, in order to achieve more efficient condensation (phase change) heat transfer. Energy implications of these choices have not been assessed.

## 3.3 Technology and projected transport capacity

We will calculate energy savings and CO<sub>2</sub> gains from using 18 MW of heat energy to provide heating for the city of Rotterdam by connecting to the transport pipe that will be built by the Warmtebedrijf Rotterdam (WBR). Technological parameters of the Warmtebedrijf heat transport system used in this chapter are from personal communication (Van Spanje, 2011).

The length of the total heat transport system of the Warmtebedrijf will be 26 km (not all of this length is applicable for the mean transport distance). There are booster stations at two points (Hoogvliet and Groene Kruisweg) where pressure is brought back at 22 bar (boosting both flow directions). The system is illustrated in Figure 6.

Figure 6 Schematic of the heat transport system



In the winter season, the volumetric flow through the transport system is expected to be approximately 1,800 m<sup>3</sup> per hour. In summer, a lower heat demand means that the flow is expected to be around 900 m<sup>3</sup> per hour. In winter, the hot stream is at 120°C and returns at 70°C, whereas during the summer, the hot stream is at 100-110 °C and returns at 58-60°C. For the calculation we have assumed a  $\Delta T$  of 50°C in winter and a  $\Delta T$  of 40°C in summer.

With the above parameters, pipeline heat demand is 101 MW in winter and 40 MW in summer. From this, it follows that when Tronox' 18 MW of steam can be fully utilized in both summer and winter, Tronox will be able to supply up to 24% of the WBR's average annual heat requirements.

### 3.4 Transport/distribution losses

Getting the heat from Tronox to the city requires some transportation with inevitable losses.

- Sizeable losses relate to the electricity requirements of the booster pumps. Of these, there are four (two locations, two directions). The average annual energy demand is calculated at about 27 mln MWh. Of which 24%, 6.4 mln MWh, is then allocated to Tronox' heat delivery.
- Other losses have to do with efficiency of the district heating system. According to the 'Protocol Uniforme Maatlat v3' (Agentschap NL, 2012), heat losses entail 6-10 GJ per house, depending on the kind of dwelling. This figure incorporates all losses due to poor insulation, conversion, etc. With an average loss of 8 GJ and an (assumed) yearly heat demand for average Rotterdam households of 39 GJ (average for a range of building types), district heating network losses are 20%.

### 3.5 Total net energy and CO<sub>2</sub> savings

Despite transportation and distribution losses, the combined effects are large savings of primary energy and CO<sub>2</sub> emissions, 24 kt of CO<sub>2</sub> emissions and 443 TJ of primary energy.

This is shown in Table 2.

Table 2 Net energy and greenhouse gas savings of providing waste heat to the city of Rotterdam

	Total WBR <sup>5</sup>	O/w Tronox	
Number of houses heated with heat from Botlek/industry	47	11	x 1,000
Net energy savings	1,828	443	TJprim/y
Net CO <sub>2</sub> savings	100	24	kt CO <sub>2</sub> /y

Uncertainties in the calculation have to do with the fraction of the amount of heat available at Tronox that will be delivered to the heat transport system, this depends on technology of heat transfer and outcome of commercial negotiations between Tronox and WBR.

<sup>5</sup> Column 'Total WBR' does not incorporate what could be done with supplied heat instead (heat from a waste incineration plant could be used to generate electricity), so is an upper limit (most positive case).





# 4 Measure ‘Separate and sell CO<sub>2</sub>/CO as products’

## 4.1 Main findings

Capturing and separating CO and CO<sub>2</sub> from the off-gas stream and selling these to industry and greenhouses, can result in large savings. Two process configurations have been calculated:

- Separating both CO<sub>2</sub> and CO, first CO<sub>2</sub> (scrubbing with amines), followed by CO using (scrubbing with toluene (COSORB)). Remaining off-gas goes through incineration and treatment. The CO is delivered to industrial clients, CO<sub>2</sub> to greenhouses.  
Possible savings of this option are 0.79 PJ of primary energy and 40 kt of CO<sub>2</sub> emissions, with large uncertainties due to week data on savings from replaced CO production.
- Separating only CO<sub>2</sub> from a purified gas stream. The CO<sub>2</sub> is captured after CO is combusted and gases have passed the gas treatment, leading to a simpler process configuration. The CO<sub>2</sub> is delivered to greenhouses.  
Possible savings are 90 TJp of energy and 2 kt of CO<sub>2</sub> emissions.

In the 1<sup>st</sup> configuration, installations for CO and CO<sub>2</sub> capture are required, in the 2<sup>nd</sup> configuration an installation for capture of CO<sub>2</sub>. Technologies for CO and CO<sub>2</sub> capture are readily available. Investments will be significant in all cases. An important factor is also the distance from the installations to pipelines for CO and/or CO<sub>2</sub>, as investments for pipelines are an important cost factor. This has not been studied in detail, but existing pipelines are located at relatively short distances from Tronox.

## 4.2 Introduction

A gas stream consisting of N<sub>2</sub>, CO<sub>2</sub>, CO and moisture currently goes to an off-gas incinerator where it is burned (together with toluene) and after this passes flue gas cleaning. The incineration of the CO fraction results in the generation of steam.

The idea of the measure is to separate the CO<sub>2</sub> and CO using suitable capture systems and sell these gases as purified products. For the pure CO<sub>2</sub> there is demand in greenhouse applications. The CO can be sold to industry that uses it in the production of syngas derived products (examples methanol, phosgene, acetic acid, etc.). Two possible configurations have been analysed:

- Case 1 - Separation of both CO<sub>2</sub> and CO and sale as purified products.
- Case 2 - CO<sub>2</sub> separation from a treated gas stream and sale to greenhouses.

In the first configuration, CO<sub>2</sub> and CO are separated from untreated off-gas. First the CO<sub>2</sub> is separated from the gas stream, then the remainder of the gas stream goes through a drying step and finally the CO is removed as a pure product. The remaining off-gas goes to waste gas treatment.

In the second configuration, the CO<sub>2</sub> separation step comes after the incinerator and flue gas treatment. Available CO is combusted first and used in generating steam. In this configuration, degeneration of the amine solvent is expected to be less because the flue gas stream is purified first.



All cases involve an extra use of energy at Tronox for the separation units. Gains and savings occur in other companies: in the greenhouses due to savings of natural gas, and at the CO-producing installation where CO from Tronox replaces other production. The extra energy use at Tronox is needed for the regeneration steps of absorbents (using steam), as well as electricity for ventilators and gas compression. In Case 1, the CO is not used anymore for its fuel value, meaning additional steam has to be generated from other fuels or purchased from a third party.

We will detail the separation technology in Section 4.3 and discuss the net overall effects of the measures in Section 4.4.

## 4.3 Separation technology

There are a number of options for separating CO and CO<sub>2</sub> from gases: chemical or physical absorption (solvent-based) or adsorption (solids-based); cryogenic distillation, and membrane separation. Cryogenic distillation would be ideal as it would allow for separation of both CO and CO<sub>2</sub> in a single step, however the presence of nitrogen is problematic and the gas needs to be very dry as well. Membrane separation is a technology in development and only works well with significant gas pressures at limited volumetric flows.

### 4.3.1 Separating carbon dioxide (CO<sub>2</sub>)

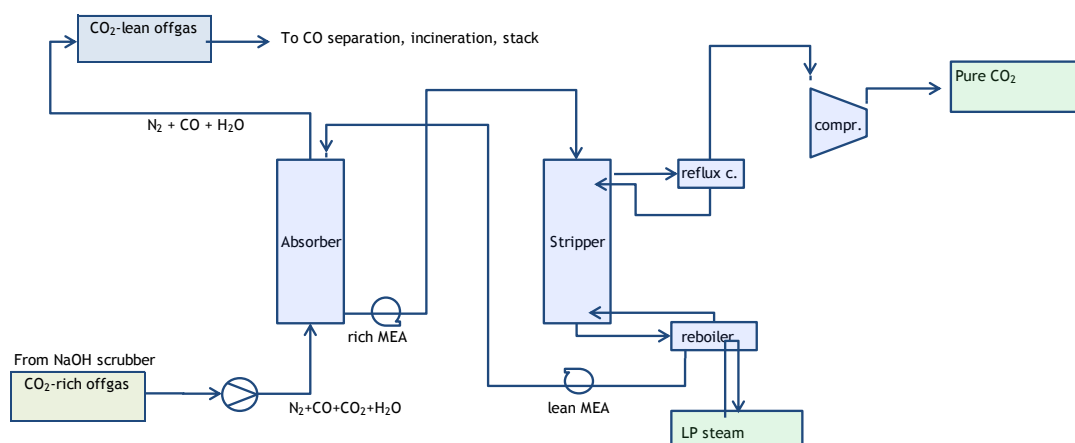
Best proven technology for capturing CO<sub>2</sub> from flue gas streams is scrubbing with an aqueous solution of alkanolamines, such as MEA (monoethanolamine). For CO removal a separate step is then required, see Section 4.3.2.

Actual removal efficiency depends on the used solvent. For CO<sub>2</sub> separation a 30 wt% MEA (monoethanolamine) solution with a corrosion inhibitor and stabiliser is commonly used. The additives are needed to prevent degradation of the solvent due to sulphur containing impurities in the flue gases. A MEA solution has a good CO<sub>2</sub> absorption efficiency of about 90%. Amine based solvents are selective for sour gases; as CO<sub>2</sub> is more stronger acidic compared to CO, the CO is not removed and still present in the gas stream leaving the absorber.

The process configuration is shown in Figure 7. The CO/CO<sub>2</sub> containing off-gas stream goes through the absorbent, where a high proportion of CO<sub>2</sub> is absorbed in the solvent. The rich solution is regenerated in a stripper with reboiler where absorbed gases are released. The CO<sub>2</sub> is dried and compressed to target pressure in a number of stages.



Figure 7 Process diagram for CO<sub>2</sub> separation from off-gas



Energy requirements for CO<sub>2</sub> removal systems are high. They vary depending on the design of the system. We have calculated with parameters of the Fluor Daniel Econamine FG plus removal system, based on IEA (2004)<sup>6</sup>.

The main energy input of the Fluoramine process is a heat input of 3.5 MJ per kg CO<sub>2</sub> removed for the regeneration of the MEA absorbent<sup>7</sup>.

There are additional energy requirements: electricity for compression of the CO<sub>2</sub> gas stream and other utility energy.

- Electricity input for CO<sub>2</sub> compression is calculated for three stage compression from 1.5 to 30 bar with intercooling and drying. If less pressure is needed this will be proportionally lower.
- Electricity for flue gas ventilation is calculated based on a pressure drop of 15 kPa at the absorber.
- The electricity demand for the MEA pumps is estimated according to (IEA, 2004).

As the MEA degrades due to impurities and sulphur containing compounds, there is a MEA consumption. The energy impacts of this use have not been calculated.

#### 4.3.2 Separation of carbon monoxide (CO)

As CO is not absorbed in a MEA solution, a different process must be used for CO-absorption. There are two options, both of which are considered proven technology.

- COSORB process, suitable for selective removal (99%) from carbon monoxide from a N<sub>2</sub>/CO/CO<sub>2</sub> containing gas stream. The COSORB process uses a liquid solvent to absorb the CO. The absorbent is on the basis of toluene, CO adheres to a Cu-Al-Toluene complex. The process layout is similar to the absorber/stripper configuration used in the CO<sub>2</sub> capture. The gas needs to be dry, so a drying step is incorporated, this can also be an absorber/stripper configuration with a glycol (TEG). Approximately 11 commercial COSORB units are operational worldwide with input gas flow capacities up to 5,500 Nm<sup>3</sup>/h, the parameters of the COSORB process are:

<sup>6</sup> IEA, 2004. Improvements in power generation with post-combustion capture of CO<sub>2</sub>, report PH4/33, Nov. 2004.

<sup>7</sup> Based on process design for Econamine unit for a 345 MW thermal power station. From the heat demand, 1.9 MJ/kg is for the reaction enthalpy of MEA-CO<sub>2</sub> release and ca. 1.5 MJ/kg for water evaporation losses and heating the rich feed.

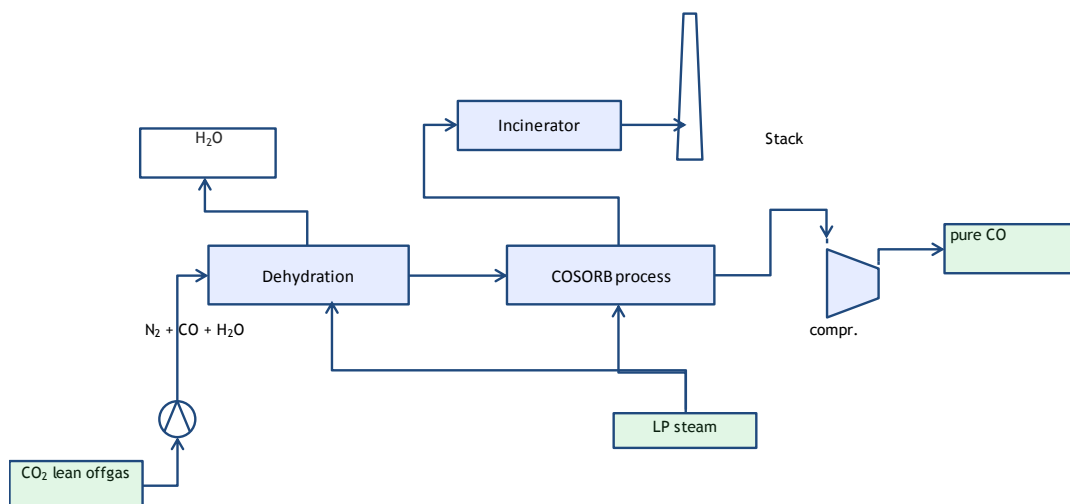


electrical power 0.2-0.5 kW/Nm<sup>3</sup> of CO recovered (range depending on climate), and reboiler heat 1.0 MJ/Nm<sup>3</sup> CO<sup>8</sup>.

- Kobelco CO-PSA process. This process uses pressure swing absorption to a Cu-Al compound. It is operational for CO production from coke oven gas (Kobe steel works), which is an application similar to Tronox. Four units have been built by Kobe steel, the largest handles 1,400 Nm<sup>3</sup>/h.

The COSORB process needs a dehydration step (for example with first a cooling step and then dehydration with TEG). A configuration is shown in Figure 8. For these, energy data are estimated and contain uncertainties. Compression is assumed to be done to 30 bar (just as with CO<sub>2</sub>).

Figure 8 Process schema for CO separation



### Extra steam from other fuels

If the carbon monoxide is separated, it is not available anymore to generate heat. In this case, HP steam has to be generated from other fuels or purchased from a third party. This entails about 170 TJ of primary energy and 10 kt of CO<sub>2</sub> emissions.

## 4.4 Effects of measures

### 4.4.1 Case 1 - Separation and sale as purified products of both CO and CO<sub>2</sub>

Additional energy requirements for the CO and CO<sub>2</sub> separation units at the Tronox site are given in Table 3.

<sup>8</sup> KTI, 1988, A. Keller and R. Schendel: *The use of COSORB II to recover high purity carbon monoxide from a feed gas*. Denver, CO: 1988; <http://www.rschendel.com/PDF/COSORB.pdf>.



Table 3 Energy and CO<sub>2</sub> consequences of measure for Tronox site

Installation part	Electricity (1,000 MWh/year)	Steam (TJ/year)
CO <sub>2</sub> separation unit	4.4	155
Off-gas drying	0.3	11
CO separation	3.3	13
Steam production replacing steam generated from CO		155
Total energy requirements	7.9	333

If low grade steam suitable for the CO<sub>2</sub> and CO separation units is readily available and currently unused, it can be used without additional CO<sub>2</sub> or energy consequences. In this case the use of steam indicated in Table 3 would not require additional energy use.

### Savings at third party CO or synthesis gas production

If CO is separated at Tronox and can be used as a replacement for carbon monoxide that would otherwise have to be produced especially, a large energy saving will result. Although the Ecoinvent data for CO production contain large uncertainties, we will calculate with this figure.

On the basis of the Ecoinvent figure, the primary energy demand of the production of CO would be 0.95 PJ<sub>p</sub>, with associated CO<sub>2</sub> emissions of 55 kt CO<sub>2</sub> eq.

These values are (far) larger than the additional energy requirements at Tronox for the separation units. Therefore, a net saving would result in the product chains of the CO/synthesis gas derived products if CO can be captured and sold as product by Tronox.

### Savings at greenhouse applications

Greenhouses need a CO<sub>2</sub> facility year-round to facilitate plant growth. According to the LEI<sup>9</sup>, CO<sub>2</sub> demand at modern, energy intensive greenhouses is about 300 kg/ha/hour, mostly during daytimes. The CO<sub>2</sub> requirements mean that in absence of a CO<sub>2</sub> facility in the form of pipeline or truck delivery, boilers and CHP-plants are run also during times without heat demand.

The net energy effect of the sale of CO<sub>2</sub> from Tronox to greenhouses depends on the extent to which farmers no longer run their own CHP plants and boilers. This decision depends on both the forecasted heat demand and the needed CO<sub>2</sub>. During the summer months, heat demand is relatively limited, and during this period having a CO<sub>2</sub> facility with pure CO<sub>2</sub> means that the on-hours of boilers and CHP installations will be reduced. ECN (2006) assesses savings of at least 15% on gas consumption, on average.

For a calculation of the savings possible, we will assume that during the winter months, having a CO<sub>2</sub> facility will have no impact on the number of on-hours of combustion installations in the greenhouses. During the rest of the year, the CO<sub>2</sub> facility will have an effect on the natural gas consumption by limiting the number of on-hours of boilers and CHP installations to the moments there is a heat demand. (In winter months, the CO<sub>2</sub> from the pipeline still has an economic value and will be used, it is just not effective in reducing natural gas demand. We assume the winter months to cover 50% of the time of a year. Since seasonal storage of CO<sub>2</sub> is not practical, only a 50% share of CO<sub>2</sub> separated at Tronox will have an effect on the use of natural gas. The effect

<sup>9</sup> LEI (Landbouw Economisch Instituut), CO<sub>2</sub>-voorziening glastuinbouw 2008-2020, Vooruitblik bij toepassing 20% duurzame energie.



on the natural gas consumption by greenhouses can be a reduction of up to 12 mln Nm<sup>3</sup> per year at greenhouses<sup>10</sup>.

As approximately 30% of gas usage in greenhouses is in CHP installations, there is, however, an associated loss in electricity production of around 13 GWh/y. This electricity is then produced at the average electricity production mix with an associated primary energy demand of 110 TJ and CO<sub>2</sub> emissions of 8 kt/a, lowering the projected savings.

CO<sub>2</sub> delivered to greenhouses has an economic value. As a large greenhouse requires 20-50 tonne of CO<sub>2</sub> per week, having a reliable pipeline facility is by far the preferred route. KEMA (2009)<sup>11</sup> gives CO<sub>2</sub> cost for a number of greenhouses, for OCAP pipeline gas a greenhouse paid € 16/t in 2009; approximately the ETS CO<sub>2</sub> price at the time.

### Overview

The following table gives an overview of the combined energy and CO<sub>2</sub> effects of the option of the separation and sale as products of CO and CO<sub>2</sub>.

Table 4 Energy and CO<sub>2</sub> savings of separating and sale both CO and CO<sub>2</sub> as purified products

	Primary energy (TJp/year)	CO <sub>2</sub> emissions (kt CO <sub>2</sub> eq./year)
Energy use at Tronox: CO <sub>2</sub> separation unit	209	13
Energy use at Tronox: CO separation unit including extra steam production	239	14
Savings at replaced CO production	-947	-53
Savings at greenhouses	-279	-14
<b>Total effect</b>	<b>-777</b>	<b>-40</b>

Note: Positive values: extra energy use/CO<sub>2</sub> emissions; negative: energy/CO<sub>2</sub> savings.

#### 4.4.2 Case 2 - Separation and sale as product of only CO<sub>2</sub>

If only CO<sub>2</sub> is separated, the separation plant can be placed after flue gas cleaning, meaning the amount of CO<sub>2</sub> available is larger compared to Case 1. A benefit of this configuration is that the flue gasses will be cleaner, leading to lower degeneration of the MEA absorbent. This is both an operational and a cost advantage (not quantified).

Similar to Case 1, there are extra energy requirements at the Tronox plant for the separation, and savings at the greenhouses.

Estimations of the total additional energy requirements for the CO<sub>2</sub> separation step at Tronox are 5.7 mln MWh/year of electricity and 201 TJ/year of steam. Similar to Section 4.4.1, if low grade steam suitable for the CO<sub>2</sub> separation units absorbent regeneration is readily available and currently unused, it can be used without additional CO<sub>2</sub> or energy consequences, in which case the above steam energy requirement is not additional.

At the greenhouses the benefit will be a reduction of up to 16 mln Nm<sup>3</sup> natural gas per year. There lower operation hours of the CHP installations in the greenhouses means an associated loss in electricity production of around 17 GWh/y, which will be produced at the average electricity production mix

<sup>10</sup> Calculated with emission factor of 1.79 kg CO<sub>2</sub> per m<sup>3</sup> of natural gas.

<sup>11</sup> KEMA (2009), Eindrapport 'Winning en opslag van CO<sub>2</sub> uit WKK-rookgassen'. M. Huibers, B.A.F. in 't Groen, P. Geerdink, M. Linders. Arnhem: KEMA (2009), p. 52.



instead. The associated primary energy demand amounts to 144 TJ and extra CO<sub>2</sub> emissions of 10 kt/a. The total effects are presented in Table 5.

**Table 5** Energy and CO<sub>2</sub> savings of separating and sale of CO<sub>2</sub> as purified product

	Primary energy (TJp/year)	CO <sub>2</sub> emissions (kt CO <sub>2</sub> eq./year)
Energy use at Tronox: CO <sub>2</sub> separation unit	272	16
Savings at greenhouses	-362	-18
<b>Total effect</b>	<b>-90</b>	<b>-2</b>

Note: Positive values: extra energy use/CO<sub>2</sub> emissions; negative: energy/CO<sub>2</sub> savings.

We see that the net savings are lower than in Case 1, the separating both the CO and CO<sub>2</sub> from the off-gas. Savings are mostly on energy and to a lesser extent on CO<sub>2</sub>.

## 4.5 Discussion

In the calculation we have incorporated the steam demands for the different separation processes. For regeneration of absorbent (MEA/Cosorb/TEG), low quality steam (~150°C) generally suffices. If use can be made of true waste steam, energy and CO<sub>2</sub> emission savings can be up to 200-230 TJ and 11-13 kt CO<sub>2</sub> higher, respectively.

For the greenhouses, an important long-term effect of CO<sub>2</sub> delivery is making a transition to supply of renewable energy possible. Farmers that want to switch to non-fossil energy systems (geothermal energy) need a source of CO<sub>2</sub> in order to do so. In the prognosis of the LEI, demand for CO<sub>2</sub> in greenhouses will be 1,550 kt/year in 2020 due to renewable energy gains. When CHP installations are replaced by renewable energy, the above calculation changes fundamentally, and larger savings are possible.

With the above results, there are uncertainties in both CO as well as the CO<sub>2</sub> separation.

With regards to the CO separation, there are uncertainties in the process energy data for the needed configuration at Tronox, as well as uncertainties with the production process of CO that is replaced. The combined effect is that the magnitude of uncertainty of the savings estimate is large, ca. +/- 50%. It is advisable to improve this estimate with a tailor-made calculation for the CO that is replaced in practice, using the actual feedstock.

With regards to the CO<sub>2</sub> separation, uncertainty has mainly to do with uptake by farmers and actual effect of CO<sub>2</sub> facility on the on-hours of heat/CHP installations. A literature scan did not yield definite figures. It is advisable to do more research on this aspect to improve on the accuracy of the savings estimate. In the meantime the calculations should be taken at an uncertainty level of +/- 25%.

An important factor is also the distance from the process installations to existing pipelines of CO and CO<sub>2</sub>, as investments for pipelines are an important cost-factor. This has not been studied in detail, but distances to existing pipelines appear rather small, in the range of 1 km.

Despite the lower savings in the chain, the case with only CO<sub>2</sub> separation is easier to implement technologically and has operational advantages compared to the case when also CO is captured. In all cases, implementation will cause



sizeable investments. Economic analysis should be performed to assess whether the options would be viable.





# 5 Measure 'Use of calcinated biocokes as petrocokes substitute'

## 5.1 Main findings

Replacement of petrocokes seems to be a technically viable option and:

- Would have a CO<sub>2</sub> emissions savings of approximately 90 kton/year and a fossil fuel energy use savings of 0.9 PJ/year, provided that the biocoke can be produced from residual materials, such as sawdust from sawmills.
- Could possibly be applied in an economically feasible manner.

The economic feasibility should be researched in order to understand the perspective better and more reliably.

## 5.2 Description of analysed measure

The quality of the cokes is dependent upon the proportion of hydrogen. This should be as low as possible. The cokes may only contain up to 2% mass of sulphur and a minimal ash content. Moisture cannot be present, as to prevent HCl formation through reactions of chlorine with condensate.

One possible option to limit the greenhouse gases at Tronox and the TiO<sub>2</sub> production lifecycle, could be to replace calcined petrocokes with calcined charcoal or a comparable product produced from biomass.

## 5.3 Technical feasibility

There are several examples indicating that production of 'biocokes' would be technically feasible:

- Activated carbon for flue gas cleaning and water cleaning produced from e.g. peat, wood or coconut shells can meet specification requirements. Activated carbon from biomass is produced at an industrial scale at Norit AC in Klazienaveen (C2W, 2010).
- Charcoal is used as a reducing agent in pig iron production in Brazil. The total production capacity of iron amounts to approximately 8 Mtonne per year and requires about 7 Mtonne of charcoal per year (IAB, 2011).
- Simcoa in Bunbury, Australia uses 27,000 metric tons charcoal as a reducing agent in the production of high purity silica. Simcoa uses charcoal made from jarrah wood. Jarrah is considered to provide a superior form of charcoal (low ash content, uniform grade with a high ignition temperature) (Simcoa, 2012).



Figure 9 Lurgi shaft charcoal kilns at Simcoa



Source: <http://terrapreta.bioenergylists.org/files/Gronli.pdf>.

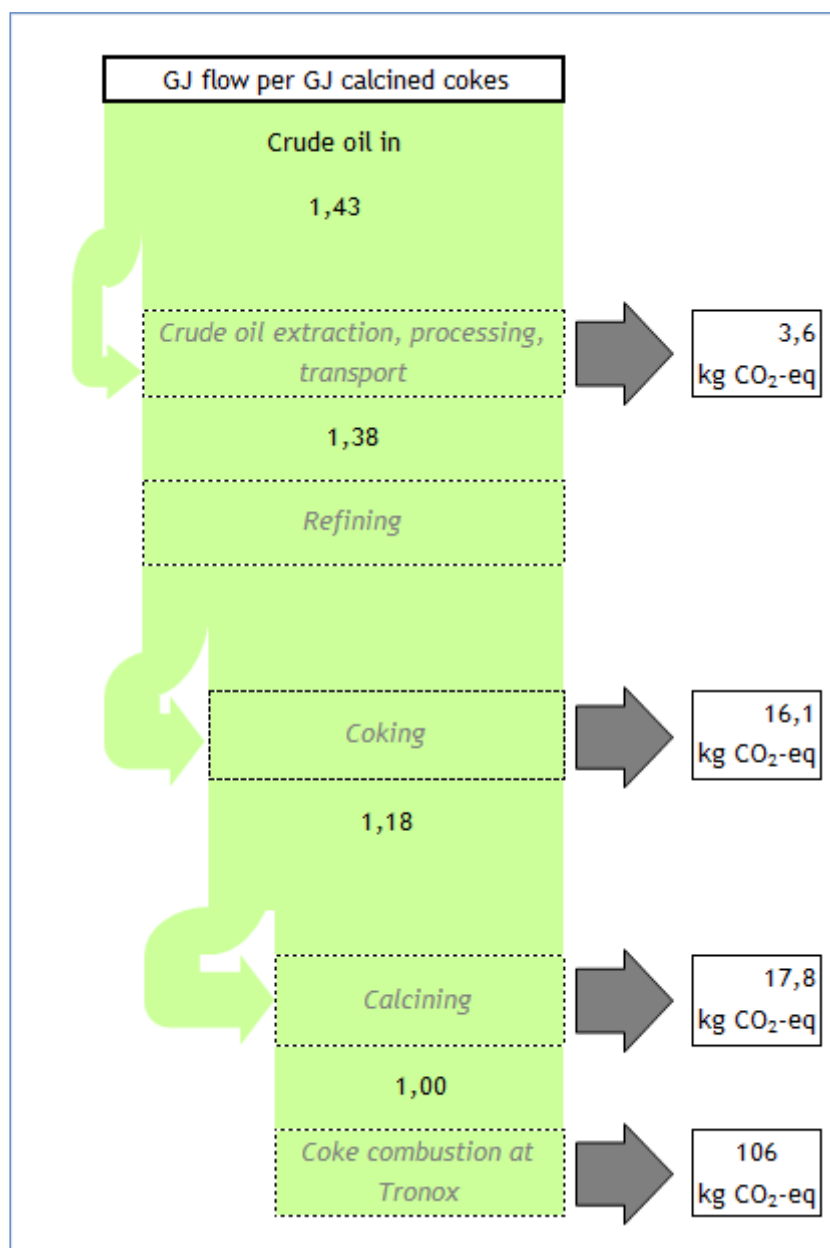
#### 5.4 Energy use and CO<sub>2</sub> emissions

The replacement of calcined petrocokes with biocoke, would result in a reduction of 1.43 GJ/GJcokes and 145 kg CO<sub>2</sub> eq./GJcokes over the entire life cycle.

##### **Substituted calcined petrocokes**

As indicated in Figure 10, the life cycle of calcined petrocokes includes all processes from extraction of crude oil to utilization of the calcined petrocokes at Tronox and the subsequent burning of product gases.

Figure 10 Sankey diagram for calcined petrocokes production (all figures in S.I. units)



Source: Own calculations.

According to JEC (2007), the extraction, processing and transport of crude oil requires 35 MJ/GJ of primary fuel and results in a CO<sub>2</sub> emission of 3.6 kg/GJ calcined cokes.

In the refinery, the crude will be distilled in atmospheric and vacuum distillation columns, leaving a residue (vacuum residue). In this analysis, it is assumed that the energy use for distillation of crude and atmospheric residue can be allocated to the distillation of the atmospheric and vacuum distillation.

The subsequent processing of the vacuum residue into green cokes has an energy efficiency of approximately 85% (Chen, 2004). The energy required for this process is covered with fuel gases produced in the conversion process. The carbon intensity of these fuel gases was assumed to be the same as that of the processed vacuum residue. Vacuum residue is also sold as heavy fuel oil for

e.g. shipping. The emission factor for heavy fuel oil amounts to 77.4 kg CO<sub>2</sub>/GJ<sup>12</sup>.

The resulting CO<sub>2</sub> emission amounts to  $(15\% \div 85\%) \times 77.4 = 13.6$  kg CO<sub>2</sub>/GJ green coke. Taking into account the energy losses in the final calcinations step (see below), this amounts to 16.1 kg/GJ calcined cokes.

The calcination of the green coke also has an energy efficiency of approximately 85% (Sunstone Development, 2011). Here too, the energy required for this process is covered with fuel gases produced in the conversion process. The carbon intensity of these fuel gases was assumed to be the same as that of the processed green cokes. The emission factor for green cokes amounts to

100.8 kg CO<sub>2</sub>/GJ. The resulting CO<sub>2</sub> emission amounts to  $(15\% \div 85\%) \times 100.8 = 17.8$  kg CO<sub>2</sub>/GJ calcined coke.

The calcined cokes itself contains approximately 98% carbon (weight, dry base) and has a lower heating value of approximately 33.8 MJ/kg. When utilized at Tronox, the cokes are completely converted into CO<sub>2</sub>, either in the chlorinators or in the off-gas incinerator (see previous chapter). The corresponding CO<sub>2</sub> emission amounts to  $(980 \times 44/12) \div 33.8 = 106$  kg CO<sub>2</sub>/GJ.

### Biocoke production

As indicated in the previous paragraph, wood can be converted into a high quality reduction agent that can be utilized in e.g. production of silicium. Based on Figure 11, yields for production of nearly pure carbon from wood were estimated to be approximately 25% in terms of weight and approximately 45% in terms of energy.

The fuel requirement for charcoal production is covered by the gaseous and volatile by-products of the charcoal production process. As biomass is a renewable energy source containing short-cycle carbon, the use of the by-products causes no net increase in the atmospheric concentration of greenhouse gases.

Processing of biomass prior to charcoal production and transports of biomass and charcoal will however produce greenhouse gas emissions.

According to the CO<sub>2</sub> tool for bioenergy from Agentschap NL<sup>13</sup>:

- Pretreatment requires 0.02 GJ/GJ wood and results in greenhouse gas emissions of 1.6 kg CO<sub>2</sub>/GJ wood.
- Transport to the Netherlands from North America has a greenhouse gas emission of 3 kg CO<sub>2</sub> eq./GJ wood and requires approximately 80 MJ/GJ of sawdust as fuel.

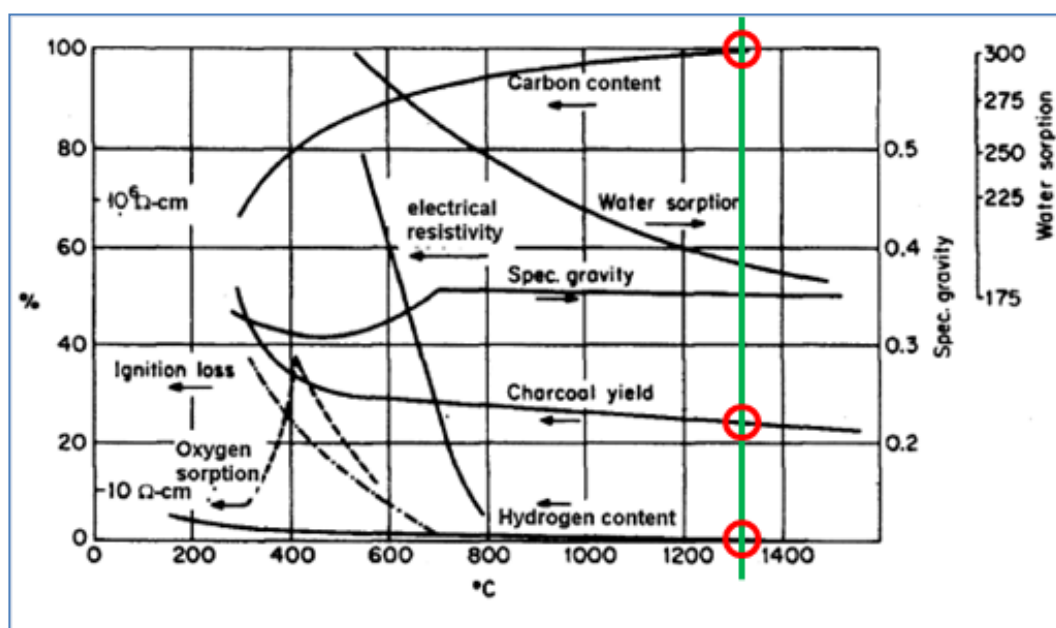
Based on these figures, the life cycle emissions for biocoke would be  $(1.6 + 3) \div 45\% = 10$  kg CO<sub>2</sub> eq./GJ<sub>biocokes</sub> and the energy use would be 0.13 GJ/GJ<sub>biocokes</sub>.

<sup>12</sup> See: 'Nederlandse lijst van energiedragers en standaard CO<sub>2</sub>-emissiefactoren, versie januari 2011'.

<sup>13</sup> See: <http://www.agentschapnl.nl/content/co2-tool>.



Figure 11 Effect of temperature on charcoal properties



Source: [http://web.1.c2.audiovideoweb.com/1c2web3536/Charcoal\\_Review%20\(iecr03\).pdf](http://web.1.c2.audiovideoweb.com/1c2web3536/Charcoal_Review%20(iecr03).pdf).

Elucidation: The line indicates the temperature considered in this study for calcination of wood charcoal and the circles indicate the parameter values used in the estimations.

### Net greenhouse gas emission saving

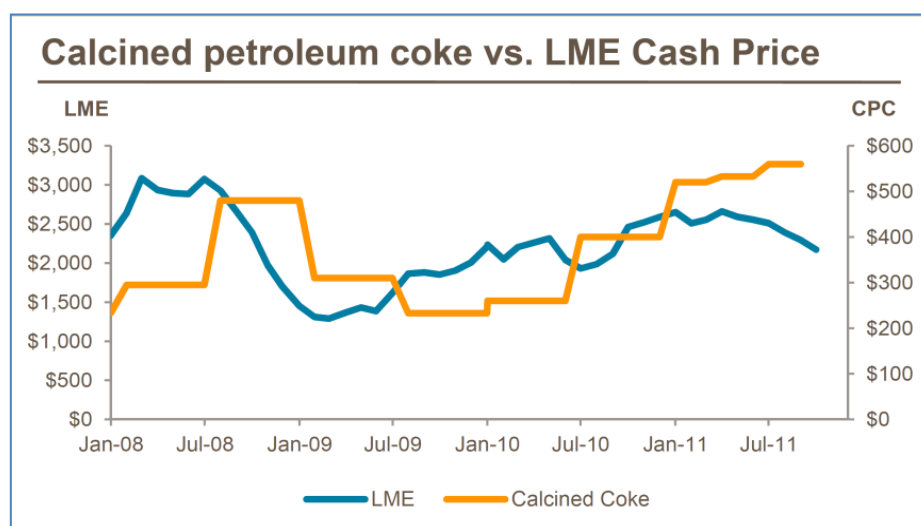
Given an aggregated life cycle greenhouse gas emission for calcined petrocokes of approximately 145 kg CO<sub>2</sub> eq./GJ cokes and an aggregated life cycle greenhouse gas emission of approximately 10 kg CO<sub>2</sub> eq./GJ biocokes and assuming that calcined petrocokes can be substituted on a 1 GJ ÷ 1 GJ basis by biocokes, the net emission reduction that can be realized by substituting calcined petrocokes by biocokes amounts to 135 kg CO<sub>2</sub> eq./GJ cokes.

## 5.5 Economic feasibility

Economically 'biocokes' may be an economically viable alternative for calcined petrocokes.

Figure 12

Development of the price of calcined petrocake



Source: [http://www.riotinto.com/documents/investors\\_databook/Chartbook.pdf](http://www.riotinto.com/documents/investors_databook/Chartbook.pdf).

The market prices for petrocake have varied in the past three years between \$ 250/tonne or € 175/tonne and \$ 500/tonne or € 350/tonne (see Figure 12).

The comparison between the known price levels for petrocake and the estimation for biocoke, indicates that the replacement of petrocake is feasible. However, further analysis of the technology and a price breakdown is necessary in order better understand the differences.

## 5.6 EU ETS

The European CO<sub>2</sub> emission trading system might in the future also pose an economical impact on this option. At present, this system covers the CO<sub>2</sub> emissions a large range of industrial processes, and reductions of emissions has an economic value. In the present 3<sup>rd</sup> phase of the EU ETS (2013-2020), the process emissions of inorganic chemical processes, such as the use of cokes in Tronox' processes, are not included in the EU ETS. However, it should be noticed that in each new phase of the EU ETS the system covers more industrial processes. Therefore, it could be possible that in a new phase also inorganic process-emissions will be included in the system. If biomass is used in industrial processes, the emissions are excluded in the EU ETS. Therefore, in the situation that Tronox' emissions would be covered by the EU ETS, substitution of petrocokes by biocokes would result in substantial financial savings.

## 5.7 Scope

Tronox is not the only consumer of green or calcined petrocake in the Netherlands. Other consumers include Aluchemie in Rotterdam, Thermphos in Vlissingen and ESD-NiC in Farmsum. The latter company uses calcined coke.



## 5.8 Remaining questions and advice

As indicated in previous paragraphs there are several practical indications that substitution of calcined petrocokes with a similar biomass based product may be technically and economically viable.

We recommend that further research in the viability of this option is conducted.

Main issues to be elaborated in this in-depth study would be:

- The biocokes specifications as a function of applied biomass, applied conversion technologies and applied operational parameters of the applied conversion technology.
- The availability of biomass, and the environmental effects of the production.
- Insight into the storability of biocokes, e.g. level of reactivity and hydrophilicity carbon after calcination, the amount of moisture binds the material after production to use?
- Insight in the product requirements and volume requirements of the various potential customers (Tronox, Thermphos, ESD-NIC)?
- Possibilities to utilize petrocokes calcinations technology for production of biocokes, e.g. for calcinations of charcoal in existing calcinations installations.
- Business case:
  - What are the resource costs of different types of biomass?
  - What are the investment and operational costs for biocokes production, broken down by technology?
  - What is the expected development in the cost of petrocokes?

We suggest to first conduct a desk top research to give a first indication of the above mentioned issues, based on literature and contacts with parties producing or utilizing charcoal or similar products as a reducing agent in industrial processes.

The in-depth study should however also include a prove of principle test and a demonstration of the viability of the concept of biocokes production at industrial scale.







# 6 Measure ‘Use of slurry waste stream as secondary construction material’

## 6.1 Main findings

Reuse of sludge cake as a secondary building material would give a reduction of primary energy and CO<sub>2</sub> emissions of respectively 34 TJ and 1.9 kton.

Note: Results are entirely based on personally communicated information received from Tronox. No written documentation has been made available.

## 6.2 Rationale behind the measure and the considered approach

Tronox produces approximately 40 kton of slurry waste per year, consisting of metal chlorides and calcium chloride. This cake has to be landfilled as chemical waste at a substantial cost.

Tronox would like to instead market the cake as a secondary structural building material for road beds. For this application, the cake or sludge is cemented by mixing it with another unspecified residual material. Based on personally provided information the cake seems to make up 75% of the mixture and to represent approximately 8% of the road bed recipe.

The mixture of cake and second secondary building material is indicated by Tronox to have a slightly cementing and binding effect, giving enhanced carrying capacity to the road bed material. The resulting road bed mixture is indicated to be slightly ductile.

As a result of enhanced carrying capacity and ductility up to 20% less asphalt is required in road construction.

As indicated by Tronox, with the exception of the leaching of chlorine, their produced cake or sludge cake meets the soil quality requirements for secondary foundation material.

## 6.3 Energy savings estimation

In order to estimate the energy savings of utilising sludge cake as IBC building material, it was assumed that the cemented mixture is applied as a component in mixed granulate in road beds in regions with setting sensitive soils.

An average road in such an area would have following structure<sup>14</sup>:

- a layer of 325 mm thickness of mixed granulates;
- a layer of 200 mm thickness of sand;
- a layer of 127 mm thickness of asphalt.

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<sup>14</sup> See: [http://www.ce.nl/publicatie/wegen\\_met\\_fosforslak/112](http://www.ce.nl/publicatie/wegen_met_fosforslak/112).



Average refers to the average of a road constructed for 25 MPa ground pressure and a road constructed for 50 MPa ground pressure.

Mixed granulates (bulk density 1,900 kg/m<sup>3</sup>) consists primarily of secondary construction materials, such as crusher granules. For estimating energy savings it was assumed that substitution of this kind of secondary building materials with cemented mixture has no or a neglectable effect on primary energy consumption.

Assuming a similar road bed structure for roads in which the cemented mixture is applied as in standard roads, the only effect to take into account is the reduction in the applied amount of asphalt.

Data for the calculation of the estimated associated energy savings are given in Table 6.

**Table 6** Data for calculation of reduction in use of fossil energy and reduction of GHG emissions in the use of slurry as a secondary building material

Bulk density of mixed granules	1,900 kg/m <sup>3</sup>
Thickness of layer	0.325 m
Surface per ton of cake =	27.0 m <sup>2</sup>
Bulk density Asphalt	2,500 kg/m <sup>3</sup>
Thickness of layer	0.127 m
Reduction in applied asphalt	20%
Energy-consumption asphalt manufacturing	320 MJ/mt cake

This results in a reduction in the use of primary energy of 34.3 TJ/year and a reduction of CO<sub>2</sub> emissions of 1.9 kton CO<sub>2</sub>/year.



# 7 Evaluation of measures

## 7.1 Overview of potential energy savings and CO<sub>2</sub> emission reductions

Table 7 shows the total calculated potentials for energy savings and prevention of CO<sub>2</sub> emissions, with an indication of the uncertainty in the calculated values.

Table 7 Overview of calculated energy and greenhouse gas savings

Measure	Primary energy savings (TJp/year)	CO <sub>2</sub> emissions savings (kt CO <sub>2</sub> eq./year)	Uncertainty	Conditions/ remarks
Purify HCl and sell as product	60	3	± 20%	Based on energy use for reference production of HCl
Use of waste heat for city district heating	440	24	± 10%	The figure is a maximum.
Separate and sell CO <sub>2</sub> and CO as products: CO <sub>2</sub> to greenhouse farmers	27	0,5	± 30%	Possible savings 68 TJp and 4 kt higher when waste steam utilised. Uncertainty in assumption on effect heat installations.
Separate and sell CO as product to industry	317	17	± 30%	Possible savings 30 TJp and 1,7 kt higher when waste steam utilised. Uncertainty in data on CO manufacture.
Use of calcinated biocokes as petrocokes substitute	900	92	± 20%	Calculated with waste material if the wood industry (saw dust) as a feed stock for biocokes
Use of slurry waste stream as secondary construction material	35	2	± 10%	
<b>Total savings potential</b>	<b>1.5 PJ</b>	<b>120 kton</b>	<b>± 25%</b>	

Based on energy use for reference production of HCl.

The total savings potential is very large: 1.5 PJ<sup>15</sup> of potential energy savings in the chain.

Even if chain energy savings should be booked on more than one party, a significant savings benefit will accrue to Tronox.

<sup>15</sup> Peta joule, equal to one thousand terajoule (one million gigajoules).



## Impact on GHG-footprint of titaniumdioxide

According to information from Tronox, typically the GHG-footprint of titaniumdioxide (chloride-process) is in the range of 6 tonnes CO<sub>2</sub>/ton TiO<sub>2</sub>. The measures contribute as follows to reduction of this GHG-footprint: Overall, the measures in the chain could amount to a reduction of the GHG-footprint with app. 25%. It should be noted that these figures are based on first estimates, and incorporate substantial uncertainties.

Table 8 Contribution of measures to GHG footprint of TiO<sub>2</sub>

Measure	Contribution to GHG footprint TiO <sub>2</sub> (indicative values)
1. Purify HCl and sell as product	0.6
2. Use of waste heat for city district heating	5.1
3a. Separate and sell CO <sub>2</sub> to greenhouse farmers	0.1
3b. Separate and sell CO as product to industry	3.6
4. Use of calcinated biocokes as petrocokes substitute	20
5. Use of slurry waste stream as secondary construction material	0.4
<b>Total savings potential</b>	<b>25%</b>

## 7.2 Technical and economical evaluation

The measures have been evaluated with representatives of Tronox in order to prioritise them. In this evaluation critical parameters are technical and economical feasibility. The evaluation results in the following picture:

- *Purification and sale of HCl*  
The technology for purification of HCl is available, and sales might be interesting from a commercial perspective, although it should be noted that parties in the market signal that commercial prices of HCl are relatively low and that there is strong competition on this market. A key factor is whether other parties will be interested in participating, and an acceptable business case can be developed. Within this study potential other candidates have been identified. With these Tronox could investigate whether an attractive business case can be developed.
- *Use of waste heat for city district heating*  
Delivery of waste heat for city district heating appears technically feasible and will result in substantial energy saving. However, investments will be large and it is unclear whether these will meet Tronox' investments criteria. This option is part of further feasibility research within Tronox.
- *Separation and sale of CO<sub>2</sub> and CO*  
CO separation is a proven technology, but requires large investments, and it is uncertain whether in the Rotterdam industrial area other companies will be interested in purchase.  
Also for CO<sub>2</sub>, separation will require large investments. In general, it can be expected that there will be a demand in greenhouses, but the economics will be a critical factor.  
Regarding the high investments and uncertainty of interest from clients, these options might be less interesting for Tronox.



– *Use of calcinated biocokes as petrocokes substitute*

The use of biocokes might be an interesting future option regarding the increasing prices of petrocokes. Furthermore, the present study indicates a very substantial impact of this option in reducing energy use and CO<sub>2</sub> emissions.

Use of biocokes in TiO<sub>2</sub> production is not yet a proven technology. However, suppliers of charcoal indicate that it might be technologically feasible, and in other reduction processes (SiO<sub>2</sub> production) it is applied on an industrial scale.

Although this is not the core business of Tronox, this option is regarded as a potential interesting future development. An option is to investigate feasibility further together with other companies in the production chain of biocokes. Contact have been made with Norit (potential producer of biocokes) which is interested in cooperation.

A first step might be to conduct within the framework of the Routekaart Chemie a further investigation on this option, in cooperation with Norit and other chemical industries which use cokes in their production processes.

– *Use of slurry waste as secondary building material*

Use of slurry waste streams as a secondary building material is a clear priority for Tronox, as the present disposal of this waste stream is expensive. The option of using the materials as a building material for motorways could avoid these large costs. Furthermore, this might result in energy and material savings in the production chains. According to information from Tronox, the use of the material will only result in (limited) leakage of chloride, which probably will not be an environmental issue in the saline environment of the Maasvlakte I and II.

Tronox has taken the initiative with van Gansewinkel to apply at the national government for a 'Green Deal'. Within a 'Green Deal', the energy savings in the use of products as secondary building material, might be an important additional argument.

The measures identified are scored in Table 9.



Table 9 Evaluation of measures

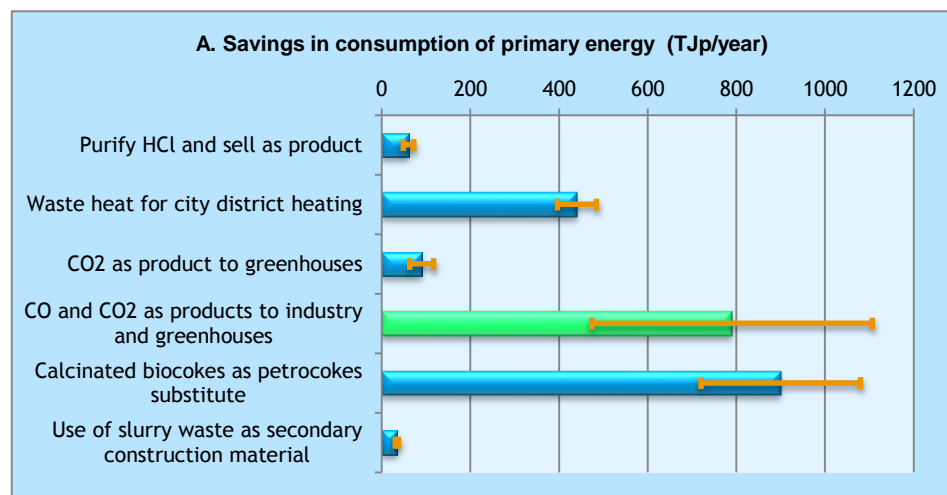
	Technical feasible	Economical feasible	Environmental impact	Potential action of Tronox
Purify HCl and sell as product	Yes	Potentially	Limited	Contact with other parties interested
Use of waste heat for city district heating	Probably	Potentially	Large	Continuation of feasibility study
Separate and sell CO <sub>2</sub> and CO as products: CO <sub>2</sub> to greenhouse farmers	Probably	Probably not	Large	None
Use of calcinated biocokes as petrocokes substitute	Not yet proven	Potentially	Very large	Contribution in feasibility study within the Framework of the Routekaart Chemie
Use of slurry waste stream as secondary construction material	Yes	Yes	Present, limited	Green Deal



# 8 Conclusions

- This investigation is directed at identifying options for energy savings in the production chains of Tronox. Points of attention are energy savings in the use of raw materials, reuse of rest materials in waste streams (solid waste streams as well as emissions to air and water), and the use of waste streams of energy.
- The investigation should be characterised as a 1<sup>st</sup> assessment of potential options. For the options identified the environmental impact has been assessed in terms of (fossil) energy savings and CO<sub>2</sub> emissions. In addition a 1<sup>st</sup> indication is given of technological and economical feasibility.
- Five measures have been identified:
  1. Extraction and sale of HCl from waste water stream.
  2. Heat delivery to the municipality of Rotterdam, via the district heating pipe line of the Warmtebedrijf Rotterdam.
  3. Delivery of CO<sub>2</sub> to greenhouses, and/or CO to industrial clients.
  4. Use of biocokes in stead of petrocokes.
  5. Use of slurry as secondary building material in roads.
- Evaluation indicates that with these measures potentially substantial energy savings can be achieved. The measures with the largest impact are the use of waste heat for district heating, the separation and sale of CO and CO<sub>2</sub>, and the use of calcined cokes as petrocokes substitute. The potential energy savings are summarized in Figure 13. Overall, these savings amount to 1.5 PJp<sup>16</sup>. This is comparable to the energy use of app. 20,000 residential houses.

Figure 13 Primary energy savings



<sup>16</sup> Note: In this calculation, for CO/CO<sub>2</sub> the 3<sup>rd</sup> option (sale of CO<sub>2</sub> to greenhouses) is taken into account (and not the alternative 4<sup>th</sup> option).



- Potential CO<sub>2</sub> emission reductions amount to 120 kton CO<sub>2</sub>. Also for this issue, use of waste heat for district heating, use and sale of CO/CO<sub>2</sub> and replacement of petrocokes by biocokes are the measures with the largest impact.

Respective to the GHG emissions in the production chain of TiO<sub>2</sub> (with a typical value of 6 kg CO<sub>2</sub>/kg TiO<sub>2</sub>), this amounts to a potential saving of 25%.





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