XMercury
– Mercury Removal System Using a Split Preheater –
First Experiences in the Cement Industry

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The UNEP Minamata Agreement of 2013 has set itself the goal of reducing mercury emissions worldwide. The name comes from incidents in Minamata, Japan, where in the 1950s, about 3,000 people died of mercury poisoning due to the discharge of mercury-containing wastewater into the sea.

Among the most important emitters of mercury, as identified in the agreement, are the artisanal gold mining and coal-fired power plants as well as the cement industry.

Although mercury is one of the rare elements in the earth's crust, it enters in various amounts and as various compounds through the fuels and mineral raw materials of primary origin needed for cement clinker manufacturing process. Due to the peculiarities of the cement manufacturing process, a mercury cycle is formed, which enriches the mercury in the process.

Therefore, in many cases, compliance with limit values is hardly possible without the use of alternative fuels and raw materials, and measures are needed to reduce emissions.

Occasionally, the cement industry uses processes that can reduce mercury emissions to their current limits. The disadvantage of these methods, however, lies in high investment and operating costs.

For this reason the companies Scheuch GmbH, w & p Zement GmbH and A TEC Produktions- und Service GmbH in cooperation have developed a new, economical process for the reduction of mercury emissions.

1. Explanation of the cement manufacturing process and substance circuits

The common method for the production of cement clinker is the so-called dry process where the raw materials are burned in a rotary kiln with upstream cyclone heat exchangers. Here, the raw material - which consists mainly of $CaCO_3$ and CaO - obtained in the quarry will be processed in a preceding mill to a finely grinded raw meal. The raw meal will be fed into the cyclone heat exchanger and passes the rotary kiln at temperatures up to 1,450 °C. During this burning process, the different clinker phases are formed, which are later responsible for the hydraulic properties of the cement.

Figure 1 shows a simplified schematic drawing of the cement clinker manufacturing process.

The temperatures in the process cover a wide range. The combustion and process gases reach up to 2,000 °C in the area of the furnace flame and cool down in counter-current when preheating the raw material to approximately 120 °C. In return, the raw material, dust and clinker are heated up to 1,450 °C in the sintering zones of the furnace.

Due to the countercurrent flow of gases and raw material, acidic gas components such as SO_2, HCl or HF [2] are bound to the solid and thus released only to a small extent through the stack [8].

This basic principle can also be applied to other elements that volatilize at the temperatures occurring during the firing process: they evaporate at high temperatures during the burning process and condense again or will be partially chemically bound to the raw-meal particles at lower temperatures.

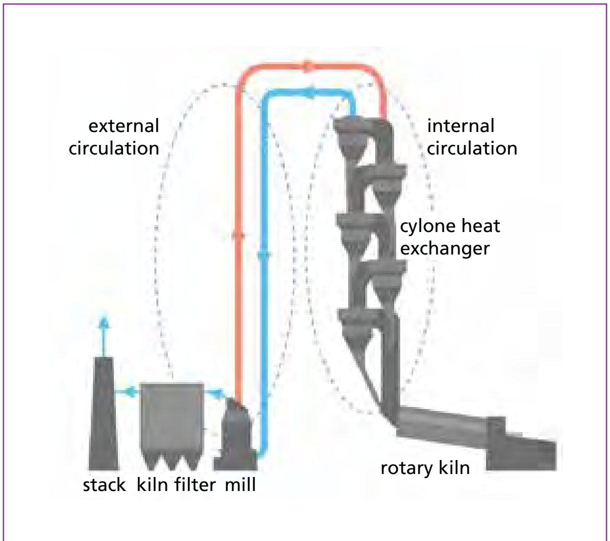


Figure 1:

Schematic drawing of the cement clinker production process with internal and external circulation

Source: Salzer, F.; Flachberger, H: Xmercury – Ein innovatives Verfahren zur Reduktion von Quecksilberemissionen bei der Herstellung von Zementklinker, Tagungsband zur 13. Recy & DepoTech (2016), 2015, pp. 215-220

Depending on the temperatures at which the volatilization or condensation takes place, a distinction is made between two different types of circuits. These are referred to internal or external circulation (Figure 1).

The internal circulation is a cycle that is formed between the kiln and the preheating tower. In this case, low-volatility inorganic substances evaporate at high temperatures in the area of the preheating tower or rotary kiln and condense again in the cooler zones of the preheating tower at lower temperatures. Due to the high surface availability, the condensed substances are adsorbed or chemically bound to the raw meal particles. As a result of this binding to the raw material, these substances once again enter the hot zones, where they at least partially evaporate again. Hence, the internal circulation is closed and there is an enrichment of the affected substances between the furnace and preheater tower. The internal circulation contains essential elements/compounds such as e.g. lead and cadmium and alkali metals that react with the available chlorides or sulfates.

The internal circuit has to be distinguished from the external circuit, which builds up between cyclone heat exchanger and mill respectively dust filter system. Some volatile elements/compounds may already evaporate at lower temperatures which prevail in the upper stages of the preheat tower and condense in the mill or filter. These components therefore accumulate in the ground raw meal and filter dust. Since the filter dust is returned into the process together with the raw meal, these substances are also recycled and there is a closure of the external circulation. Typically, the substances that are in the outer cycle are volatile heavy metals such as mercury or thallium.

If the raw mill is in operation, which is also referred to as *compound operation*, the kiln exhaust gas is used to dry the raw material in the mill. Therefore, the gas passes the filter at low temperatures (about 120 °C) and the sorption of the substances on the raw meal works better. In addition, more surface is offered by the higher amount of raw meal which additionally increases the sorption capacity.

When the mill is switched off (*direct mode*), the exhaust gas is led directly into the filter after passing a separate cooling stage. The sorption is therefore limited only to the kiln filter and runs off at lower dust loads. In addition, higher temperatures – approximately 180 °C – prevail during direct operation, which also reduces the sorption capacity.

On average, cement plants worldwide operate in compound mode between 80-90 % of the operating hours [3], therefore this operating state is used for further consideration and description.

Since mercury is omnipresent in the earth's crust in low concentrations, the sources of mercury in cement clinker production are the raw materials and the fuels [5, 6, 4, 1].

In addition to elemental mercury, various components present in the flue gas of the clinker production process oxidise mercury and form various compounds [8].

The melting, boiling and sublimation temperatures of these compounds are shown in Table 1.

compound	melting point	evaporation point	sublimation temperature
	°C		
Hg(0)	-39	357	n.a.
$HgCl_2$	277	302	n.a.
HgS	n.a.	446–583	580
HgO	n.a.	356	500
$HgBr_2$	237	322	n.a.
HgI_2	259	350	n.a.
HgF_2	645	650	645

Source: Perry, R. H.; Green, D. W.; Maloney, J. O.: Perry's chemical engineers' handbook, 7th ed. The McGraw-Hill Companies Inc., 1997

Table 1:

Melting, evaporating and sublimation temperatures of various Hg compounds

A typical mercury cycle in cement clinker production is shown in Figure 2. The mercury compounds are fed in via the raw material or the fuel evaporate in the clinker burning process and condense again in the mill or kiln filter. Due to this cycle, enrichment of mercury occurs, whereby the highest mercury concentration occurs in between raw meal silo and clinker burning process.

If the cycle is saturated or the temperature at the filter is increased, the mercury can no longer be efficiently adsorbed and bound on the filter dust and consequently it leads to increased emissions which culminates in a possible exceeding of the limit.

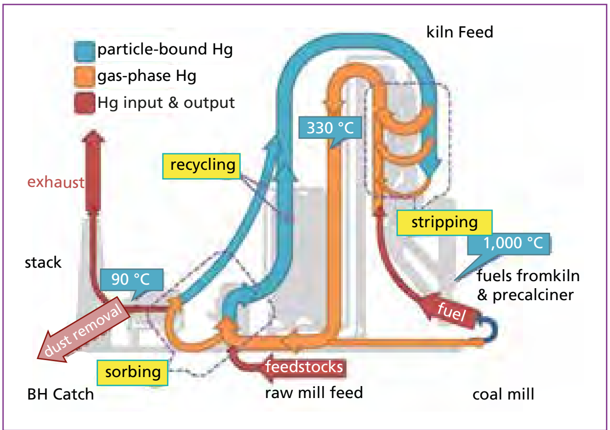


Figure 2:

Typical mercury cycle of a cement clinker production plant

Source: Sikkema, J.K.: Fate and transport of mercury in Portland cement manufacturing facilities. Graduate Theses and Dissertation, Iowa State University; USA, Paper 11907, 2011

To reduce the mercury loads in the process, several options can be considered so far.

Basically, by selecting suitable raw materials and fuels, the entry of mercury into the system can be reduced.

Since the raw material is usually extracted from quarries located in the immediate vicinity of the production facility and only certain fuels (fossil and/or alternative fuels) can be used for an economical operation of the cement clinker production, this approach is not practical. This is the reason why other measures to reduce mercury emissions are recommended.

Variants for reducing the emission are the use of an activated carbon filter after the dust filter at the end of the process chain or the injection of activated carbon before the dust filter to improve the sorption in the dust filter. Both variants will require high amounts of activated carbon so that the emission at the chimney can be reduced.

In addition, considerable investment costs are associated with the variant of the activated carbon filter and when using the activated carbon injection measures must be additionally carried out to relieve the circulation

As a further variant or also in connection with the activated carbon injection into the dust filter, there is the possibility to remove a part of the filter dust. In this case, a part of the dust which contains mercury and is separated in the filter, is removed from the process. This leads to the depletion of the mercury cycle and to the reduction of the emission. It is also possible to combine this procedure with an activated carbon injection before the filter.

Depending on the level of mercury emission or the loading of the circuit, it may be necessary to remove significant amounts of dust from the process.

The discharged material, which has already been completely prepared for the clinker burning process, is therefore no longer available as a raw material for cement production and has to be treated separately or even has to be disposed.

2. Preliminary tests at the Wietersdorf site

As a first step the entire production process was calculated regarding mercury and the basic idea for the process was created. This basic idea of the XMercury is to free the filter dust, which is similar to the raw meal in its composition, from mercury and finally reintroduce this dust as raw material into the production process, without recharging the mercury cycle.

For a better understanding of the mercury cycle a number of preliminary laboratory tests and a large-scale test was executed at the Wietersdorf plant to confirm the basic idea:

In the first step, the entire filter dust was continuously discharged from the clinker production process over a period of one week.

In addition, all input and output streams of the clinker production were sampled and analyzed in order to be able to balance the entire cycle and know the mercury loads at the several points of the process. This analysis campaign included around 500 samples over the trial period.

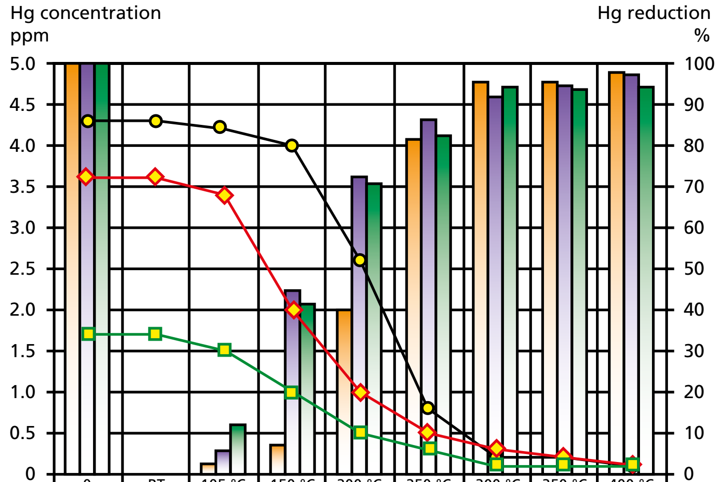
The insights gained from this experiment even exceeded expectations: the mercury cycle could be relieved more than expected and mercury emissions were therefore reduced by more than 75 %.

The accompanying analyzes also showed that the feed of mercury is equally by the raw material and the fuel.

The next step was to carry out tests on the discharged filter dust.

The chosen method for reducing the mercury concentration in the filter dust is the thermal treatment, whereby the mercury can be vaporized and in the following process steps separated from the gas phase. In principle, the thermal treatment is the same process that takes place in the preheating tower during clinker production and ultimately leads to the formation of the cycle.

In order to determine the feasibility of this procedure and the required temperature window for the evaporation, laboratory tests were carried out. The filter dust samples were heated in stages and analyzed after each temperature step. The investigations showed that most of the mercury could be separated from the samples at a temperature range of 300-350 °C (Figure 3).



		0	RT	105 °C	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C
sample 2	%	100	0	2	7	40	81	95	95	98
sample 3	%	100	0	6	44	72	86	92	94	97
sample 4	%	100	0	12	41	71	82	94	94	94
sample 2	ppm	4.3	4.3	4.2	4.0	2.6	0.8	0.2	0.2	0.1
sample 3	ppm	3.6	3.6	3.4	2.0	1.0	0.5	0.3	0.2	0.1
sample 4	ppm	1.7	1.7	1.5	1.0	0.5	0.3	0.1	0.1	0.1

Figure 3: Results of the Hg evaporation tests carried out in the laboratory

Source: Salzer, F.; Flachberger, H.: Xmercury – Ein innovatives Verfahren zur Reduktion von Quecksilberemissionen bei der Herstellung von Zementklinker, Tagungsband zur 13. Recy & DepoTech (2016), 2015, pp. 215-220

3. The development of the process

On the basis of the theoretical considerations confirmed by the experiments in Wietersdorf and the supplementary laboratory experiments, the process for mercury separation could be planned in detail and a pilot plant was designed for the use in Wietersdorf.

In the planned process, the filter dust is heated by hot kiln gases, which are taken from one of the lower cyclone stages of the preheating tower at temperatures of 800-900 °C.

The heating up of the dust takes place in the same way as in the existing preheating tower, but is carried out parallel to this. The heating process of the filter dust thus is carried out in a second strand of the preheating tower, and the preheating tower is split, so to speak.

The filter dust is heated up in this second strand of the preheating tower to the required temperature for the evaporation of the mercury. In this line, as in the existing preheating tower, high-performance cyclones are integrated, which separate the majority of the largely mercury-free dust. This approximately 350 °C hot dust is recycled directly into the main pre-heating tower, whereby the thermal energy contained in the dust also flows back directly into the process and is not lost.

After the dust separation in the high efficiency cyclones, a hot gas filter equipped with ceramic filter elements is arranged. There, the remaining dust that is still contained in the gas stream, is also separated and fed to the main preheater. Since temperatures of about 350 °C also prevail in the hot gas filter, the mercury cannot condense on the particles and remains almost completely in the gas phase. Thus, the entire filter dust is free of mercury and can be recycled as raw material in the clinker burning process. This breaks the mercury cycle and removes the mercury from the production process via a defined route.

The dust-free, mercury-loaded gas stream is then cooled by a quenching step to the temperature required for sorption. Finally a suitable sorbent (e.g. activated carbon) is injected to capture the mercury. The sorbent is separated in a second filter stage.

Experiments have shown that using a high-quality gas-phase-brominated activated carbon under optimal conditions allows almost 100 % mercury removal. For better loading and thus better utilization, the used sorbent is recirculated several times.

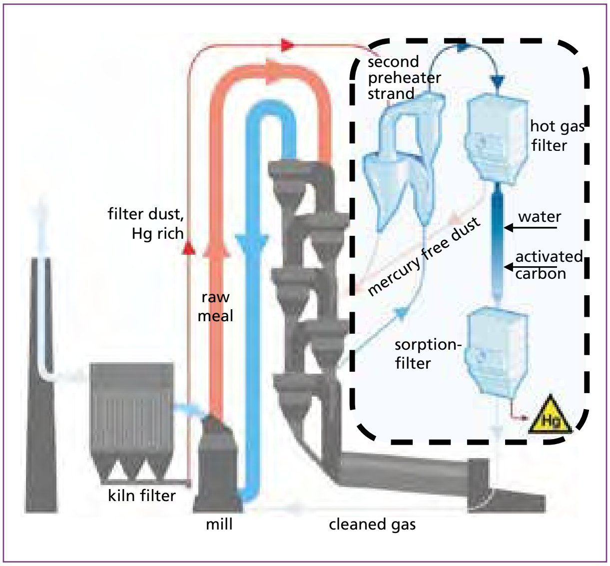


Figure 4:

Simplified illustration of the XMercury pilot plant (within the dashed line) in the clinker production process

Source: Salzer, F.; Flachberger, H.: Xmercury – Ein innovatives Verfahren zur Reduktion von Quecksilberemissionen bei der Herstellung von Zementklinker, Tagungsband zur 13. Recy & DepoTech (2016), 2015, pp. 215-220

The highly loaded sorbent is then discharged from the mercury separation plant and can be fed to a suitable disposal.

The cleaned and largely mercury-free exhaust gas flow is directed back again in front of the mill into the main exhaust stream of the clinker production process.

The system is thus fully integrated into the process, which minimizes thermal losses.

4. First operating experiences with the plants in Wietersdorf and Allmendingen

As planned, the pilot plant was implemented in the cement plant in Wietersdorf and set into operation there in April 2015.

Approximately 5-10 t/h of filter dust are treated with the XMercury, whereby the dust is heated up to about 350-400 °C.

The required amount of hot gas is about 3-5 % of the total gas flow of the kiln and is subtracted from the cyclone stage 5 of the preheater tower.

The mercury content of the filter dust which is treated in the plant is about 1 ppm.

On the other hand, the dust which is separated in the high temperatures in the high-efficient cyclones and the hot-gas filter and returned into the preheater has a mercury content of about 0.05-0.1 ppm.

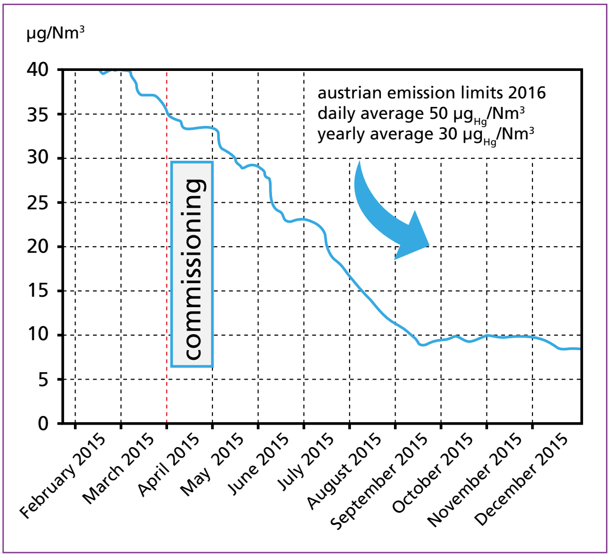


Figure 5:

Trend of Hg emission after commissioning of the pilot plant

Source: www.umwelt.wup.at

By analyzing the single dust flows regarding the mercury content it could be shown that after evaporation in the second preheater strand of the pilot plant approximately 90-95 % of the bound mercury are remaining in the gaseous phase and can be adsorbed with almost 100 % efficiency on the sorption filter.

Due to the high efficiency of the evaporation and the sorption the discharge of the mercury cycle worked better than expected after the preliminary experiments. Therefore, within a few weeks, a stationary state was already reached, in which the expected reduction in emissions could even be exceeded (Figure 5).

Currently, the plant is operated constantly with a separation efficiency of more than 80 % and emissions at the chimney can be easily maintained at values of <10 µg/Nm³ (Figure 6).

Through further optimization, the consumption of resources during the first year of testing could be significantly reduced.

The mercury content of the activated carbon has been increased from initially about 1,000 ppm to more than 5,000 ppm by selecting suitable adsorbents and adjusting the operating conditions.

As a result, the pilot plant at the Wietersdorf plant only needs a small amount of fresh sorbent and subsequently produces only a small amount of the highly mercury-loaded sorbent (maximum 10 t/a) which has to be disposed. The consumption of electrical energy of the entire system, including the transport of dust by means of pneumatic conveying, can be quantified with approximately 0.8-1 kWh/t clinker. Another advantage of the system is the direct use of heat from the clinker burning process to heat the filter dust so that no additional thermal energy has to be fed into the system.

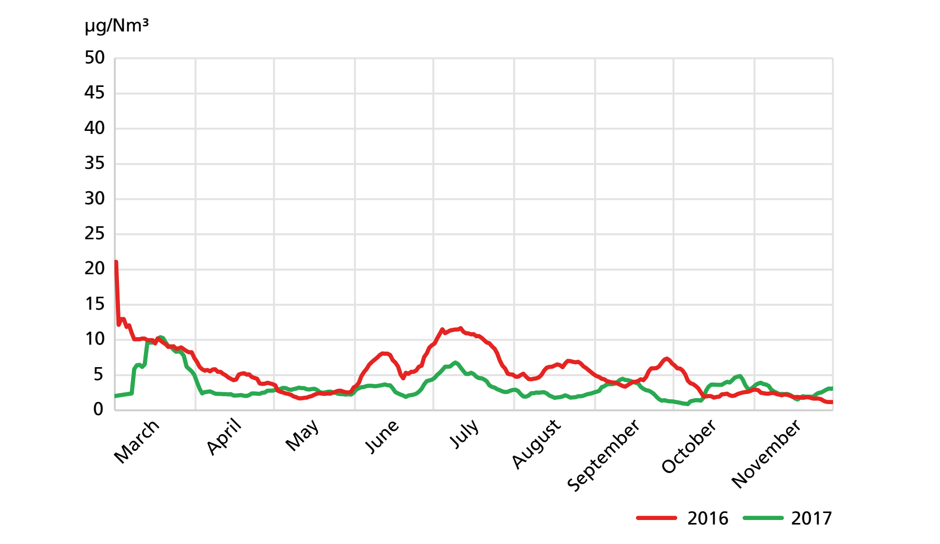


Figure 6: Hg Emission on stack, daily averages

Source: www.umwelt.wup.at

The plant for Schwenk Zement KG in Allmendingen is designed to treat approximately 12 t/h filter dust and was set into operation in May 2018.

Since the hot commissioning phase the plant is now running in stable operation and an extensive test campaign will be executed to evaluate the performance of the plant.

5. Outlook

The pilot plant delivered excellent results from the beginning on. The Hg concentration in the mercury cycle and thus also the emissions could be reduced by more than 80 %. The mercury-enriched sorbent exceeded the original expectations for mercury content (original target: 1,000 ppm) to a high extend.

Further tests on the pilot plant with different sorbents, temperatures and plant configurations led to further improvements of the plant design which resulted in minimized operating and investment costs. The unique Xmercury system is an economical solution for cement plants and can therefore contribute to reduce the mercury emissions to meet the targets of the Minamata agreement. Furthermore, collaborations with other companies are also planned in order to find a technical possibility for the reprocessing of the adsorbate, which is currently disposed.

Furthermore, the adaptation of the method to other industries (e.g. energy industry) or other substances is considered.

6. References

[1] Åmand, L.E., Leckner, B.: Metal emissions from co-combustion of sewage sludge and coal/wood in fluidized bed. Fuel 83, 2004, pp. 1803-1821.

[2] CEMBUREAU The European Cement Association: Best available technologies for the cement industry, Brussels; Belgien, 1999.

[3] Department of Environmental Quality State of Oregon: Ash grove mercury reduction, advisory committe's report, 2007.

[4] Fytili, D., Zabaniotou, A.: Utilization of sewage sludge in EU application of old and new methods-a review. Renewable and Sustainable Energy Reviews 12, 2008, pp. 116-140.

[5] Hills, L.M., Stevenson, R.W.: Mercury and lead content in raw materials. PCA R&D Serial No. 2888, 2006.

[6] Sprung, S., Rechenberg, W.: Levels of heavy metals in clinker and cement. Zement-Kalk-Gips 47, 183, 1998.

[7] VDZ Cement Paperback 2002, 50th edition

[8] Zheng, Y., Jensen, A.D., Windelin, C., Jensen, F. (2012) Review of technologies for mercury removal from flue gas from cement production processes: Progress in Energy an Combustion, Science 38, pp. 599-629

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