

Mercury Removal from Off-gases at Tinfos Manganese Plant, Øye Smelteverk, Norway

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1. ABSTRACT

In 1993 Tinfos became aware of the Hg emissions from the plant (99,2 kg in 1999). It was soon found that some Mn-ores were the main contributors to these emissions. Since then, Tinfos has tried to find a way of solving this problem. This paper describes the different strategies and processes that have been considered. An explanation is given why Tinfos has chosen the unknown/untried Miltec process, and not the other processes, already in use. The principles and the experiences of the Miltec process are outlined. All through the process Tinfos has been working in corporation with SFT (The Norwegian Pollution Control Authority). It should be mentioned that also other metallurgical plants in Norway are working with Hg-cleaning facilities.

2. GENERAL INTRODUCTION

2.1 MERCURY

The toxicological effects of mercury are indisputable. Acute poisoning often results in lung oedema and influenza like symptoms. Long time exposure may cause damages to the neural system and the brain and give rise to deformities on embryos. Both The Norwegian Pollution Control Authority and the EU have put mercury and its compounds on warning lists. Mercury is put on the Norwegian "OBS list"¹, which consist of compounds which may cause damages to health and environment, and the use and production of such should be minimised.

2.2 ABOUT TINFOS

Tinfos Manganese Plant in Kvinesdal, Norway, also known as Øye Smelteverk, was built in 1974.

Silicomanganese is the main product with an annual production capacity of 180,000 tons made up of standard, low carbon and low boron qualities. The furnaces may also produce high carbon Ferro-manganese with a production capacity of 240,000 tons per year. The silicomanganese is produced in three 45 MVA submerged arc furnaces, using Söderberg type electrodes. The third furnace came on stream the 23 rd. October 2000. This new furnace has increased the production capacity by approximately 50 %.

The off-gases from the furnace go through several steps before emission to air. The gas is washed with water in venturi scrubbers and passed through cyclones, and then the remaining CO containing gas is burned in the steam boiler of the Tinfos Thermal plant. The thermal plant recovers 10-15 % of the total initial electricity input.

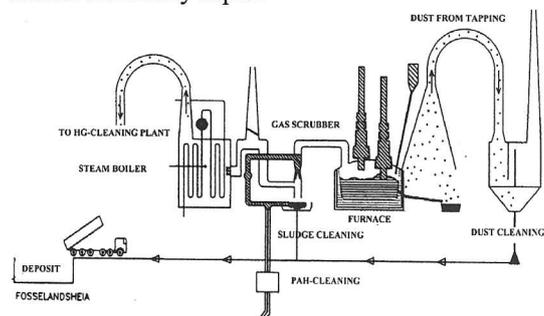


Figure 1 Layout of furnace and cleaning facilities

In 1993 Mercury (Hg) was discovered in the off-gas system at Tinfos. Soon it was found that some of the Mn-ores were the largest contributor to the Hg content in the off-gases, but also other raw materials contain Hg in various amounts. About 100 kg of Hg has been released per year to the air. The present limits do not allow more than 15 kg of Hg per year ($\sim 40 \mu\text{g}/\text{Nm}^3$) for three furnaces.

Tinfos has since 1993, in corporation and with financial support from SFT (The Norwegian Pollution Control Authority), carried out several investigations to find an effective way of removing Mercury.

3. PROCESSES FOR REDUCTION OF MERCURY EMISSIONS

Different technologies have been considered in order to solve the problem. In practice there are three main technologies available; wet scrubbing, dry-cleaning with the use of Hg-absorbing filter masses and dry cleaning with injection of active carbon and filtration on a fabric filter.

Both technical and economical aspects on the different processes have been considered. In the next chapter these technologies are presented briefly.

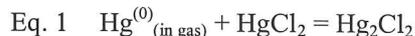
3.1 THE BOLIDEN NORZINK PROCESS,^{2,3}

At the NORZINK electrolytic zinc smelter in Odda, Norway, it was found in the late sixties that nearly all available zinc concentrates contained high amounts of mercury. When these concentrates were treated with the existing and conventional technologies, they could cause severe problems of mercury pollution. The situation was considered acute and a serious problem to the operation of the smelter. Since no proven technology was available at that time, a joint research-program was set up by Norzinc and Boliden, which is Norzinc's mother company in Sweden, to develop a solution to the problem by inventing a new technology. The Boliden/Norzink Process for Gas Treatment and Metallic Mercury Recovery came out as the most versatile and applicable alternative.

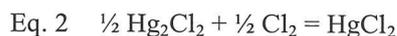
3.1.1 Process chemistry

The mercury containing off-gases (ppm-concentrations) are subjected to scrubbing treatment in specially designed reaction towers. Here the gases react with a water-based

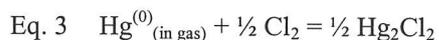
solution of dissolved mercuric chloride complexes, here denoted as HgCl_2 . When the process conditions are controlled within the prescribed ranges, elemental mercury will react nearly completely with the scrubber solution. An insoluble mercury(1)-chloride (calomel) will precipitate and then be separated as a dense slurry. The reaction can be written as:



In the next step, half of the slurry is periodically withdrawn and treated with chlorine gas for re-oxidation into mercuric form, and for regenerating and replenishing the active chloride complex of Eq. 1. The reaction can be written:

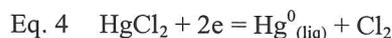


When these two reactions are added the total net reaction of the gas treatment process is obtained:



Note that there is a net consumption of chlorine gas and that an amount of calomel is produced equivalent to the mercury content in the feed-gas. This material can easily be disposed of – or it can be converted into other forms, such as liquid metal. If this is done, a waste-free plant is obtained, by an electrowinning technique.

A suitable electrolyte is produced by oxidation of all excess calomel from the gas scrubbing process, in principle as per Eq. 2 above. This electrolyte is fed to a specially designed electrowinning cell. In the process, mercury metal with a high degree of purity is produced at the cathode, whereas chlorine gas is produced by anodic oxidation.

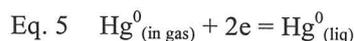


The chlorine gas is recycled for use in the calomel oxidation.

By combining the equations;



Eq. 5 is obtained



As seen, the chlorine produced from equation Eq. 4 balances the total consumption in the combined process.

This means that an autogenous process is obtained, wherein the only input is DC-energy for the electrowinning.

The performance of the process is excellent, with scrubber efficiency in the range of 99.95-99.97 %. Typical Hg content of the gas after treatment is 20-30 $\mu\text{g}/\text{Nm}^3$. The process runs at optimal condition when the gas is cooled down to 30-40°C.

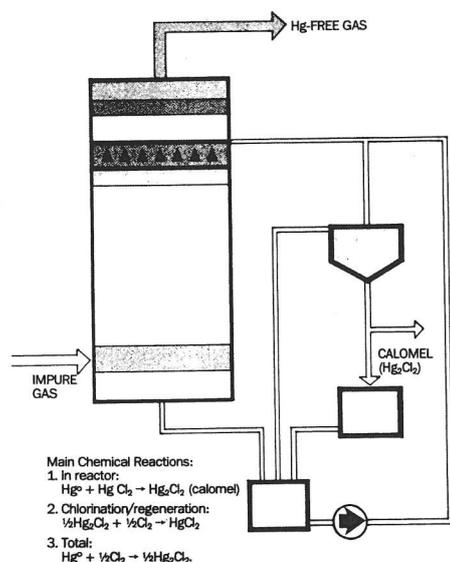


Figure 2 The Boliden-Norzinc process

3.2 SELENIUM FILTER, -SYSTEM BOLIDEN CONTEC,

The filter is specially designed to handle metallic mercury vapour at low concentrations. The filter consists of a cylindrical shell fitted with an inlet and an outlet connection. The gas is forced radially through a cylindrical layer, made up of a porous granulated material impregnated with selenium. The process is based on the reaction between metallic gaseous mercury and selenium. When the Hg-containing gas is forced through the filter, practically all the Hg present will react with selenium.

The result is a mercury-selenide, a stable mercury-compounds. This is, of course, favorable from a deposit point of view. The filter has a high capacity for Hg-absorption, typically 50-kg Hg/ m^3 filter mass. Converting the mercury to a selenide is considered to be a good solution to the problem of end deposit, this according to Swedish authorities⁴. The filters are normally designed to give the filter mass an effective life of 5-10 years. When the filter mass is saturated, it can easily

be removed and replaced. However, it can not be regenerated. It is recommended that the off gas temperature do not exceed 120°C.

Boliden Contec's selenium filters have been successfully installed at different metallurgical plants, thermal power plants, crematoria etc.

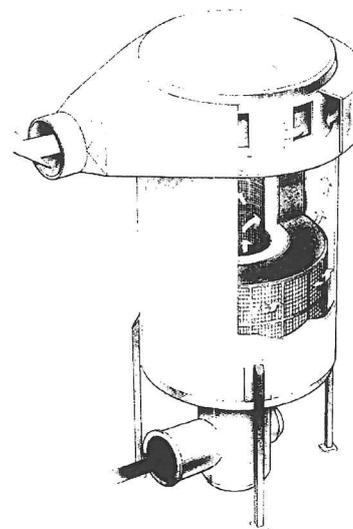


Figure 3 Selenium filter (Boliden Contech)

3.3 ACTIVE CARBON POWDER INJECTION (ABB FLÄKT)

In this process the hot off-gases, typically 100-140°C, are charged with an adjusted amount of active carbon, typically 50-100 mg/Nm^3 . The gaseous mercury is removed on the sorbing surface, in this case active carbon. The further treatment is done in fabric filters where the Hg containing active carbon is collected. The filter dust must be treated as special waste.

By combining active carbon and fabric filter, both sub-micron particles containing Hg and gaseous Hg are removed. In some cases Na_2S and lime can be added to the dry scrubber to improve the Hg removal. In such cases SO_2 , HCl, dioxins etc are also removed.

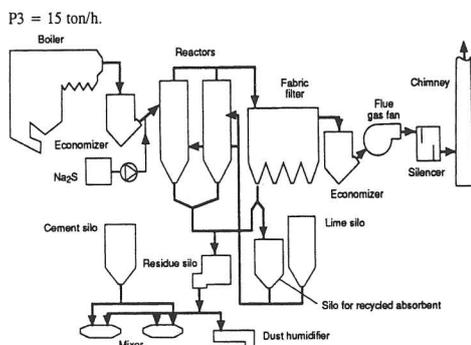


Figure 4 APC flow diagram at a waste to energy plant, delivered by ABB fläkt

3.4 THE MEDISORBON® PROCESS⁵ (LURGI BAMAG)

This process can be used to remove both mercury and dioxins from flue gases. This is done in a zeolite-based adsorber. Zeolites are crystalline alkaline aluminosilicates exhibiting a three-dimensional open lattice structure, which forms defined micropores with a closely limited pore radius distribution.

The removal of dioxins takes place by purely adsorptive mechanisms. Mercury is removed by chemisorption. To achieve this, the zeolites are impregnated with elemental sulphur. The metallic mercury vapour is absorbed and then reacts with the sulphur to form mercuric sulphide (HgS). HgS is a non-volatile water-insoluble compound. Mercury is thereby fixed. The process runs at about 60-85°C, higher temperature entails the risk of sulphur being lost from the adsorbent. Lower temperatures will result in a lower reaction rate. In order to avoid increased retention of water by the adsorbent, relative humidity of the flue gases must not exceed 85-90%. Dust concentration in the flue gas to be cleaned should not be more than 10 mg/Nm³ due to the risk of excessive pressure drop. Since zeolites are inflammable, the process has no risk of spontaneous ignition, which may be a risk using carbonaceous adsorbents. The mercury-saturated zeolite can be regenerated.

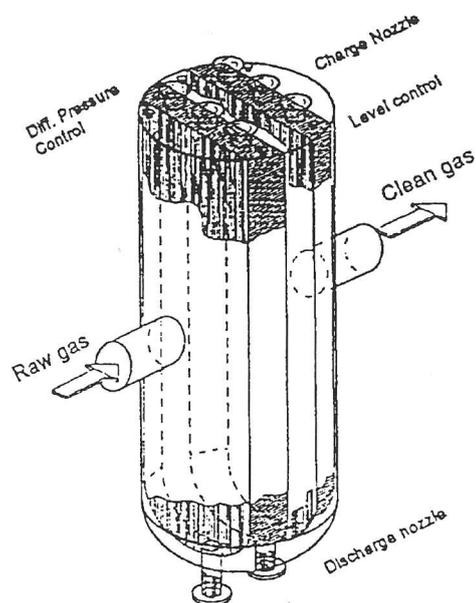


Figure 5 The MEDISORBON® process (Lurgi Bamag)

3.5 CHOICE OF PROCESS

As known, none of the different processes were chosen. This is due to the following:

- The Boliden Norzinc process has its optimum process temperature on 30-40°C. The coldest point of the off-gas system at Tinfos is 48°C. A lower temperature would have a negative effect on the PAH-removal and the solubility of CO. A gas containing dust and tar may result in clogging of the filter mass. Due to the regeneration of calomel (Hg₂Cl₂), the process is more suited for gases with a higher Hg-concentration than that of Tinfos. When the above is taken into account, the B-N process was not considered as the optimum solution to Tinfos.
- Selenium filter (Boliden-Contec), producing mercury-selenide is very well suited as a final deposit. The high stability of this end product and the small amounts of material to be deposited, makes this process promising. The relatively small filter units make it easy to install them into the existing plant. All these factors taken into consideration it was concluded that the use of selenium filters would be a very good solution for Tinfos. However, when such filters were tried in a pilot plant at Tinfos, the problems with clogging of the filter became obvious. This is

due to the amount and nature of the dust in the furnace off-gases. This was the main reason to the rejection of the selenium filter process.

- Active carbon injection (ABB fläkt). Also this process was considered to give an adequate solution to Tinfos problem, with a well-proven technology. However, the investment cost and the operation costs was expected to be higher than an equivalent selenium filter. The deposit of considerable amounts of Hg containing filter dust could be a problem from this process. Thus, the process was considered to be the second choice.

- The MEDISORBON[®] process came in to discussion at a later stage than the three other processes, and was thus not considered in the same way. It is presented here to show the variety of Hg-removal processes. However, it is obvious that the demand for low dust- and humidity-concentrations in the off-gas, could be an obstacle for the use of this process at Tinfos, as was the case for the selenium filter.

3.6 THE MILTEC PROCESS*

In addition to the search for new cleaning technologies, the ore supplier has investigated methods of pre-removing mercury from the ore.

However, these efforts and the existing technology have so far proven to be insufficient in order to meet the levels of emissions set by SFT, of 15 kg Hg/year from 2001.

Thus, Tinfos and the Norwegian Company Miltec have developed a new cleaning technology. Pilot experiments have given an 85 % reduction of emissions⁶. Since the start up of the full-scale operation in April 2000, similar, and even better results have been obtained

3.6.1 PROCESS CHEMISTRY AND TECHNOLOGY

The process gases contain gaseous mercury (Hg⁰), SO₂, H₂, CO, CO₂, H₂O and N₂. In addition the gas contain some dust in which mercury-sulphides (HgS) and metal-amalgam (MeHg) are present. As mentioned before the process gases are burned in a steam boiler at

* The MILTEC Process is patented in Norway, and patent pending in Europe, US and Canada

the Tinfos thermal power plant. This is done with a surplus of oxygen. The combusted gas contains negligible amounts of CO and H₂. Nearly all mercury entering the furnace follows the off-gas stream. Some mercury is deposited in the piping, but these amounts are taken out during the periodically cleaning of the off-gas piping system.

By burning the gas with air the amount of gas increases from about 8 000 Nm³ per furnace per hour to about 24 000 Nm³ per furnace per hour. The Hg concentration of the exhaust gas is about 280 µg/Nm³. Due to the removal of CO from the gas, the following gas treatment is made easier, due to a non-explosion risk gas.

The combusted gas is scrubbed in a wet gas-scrubber as follows:

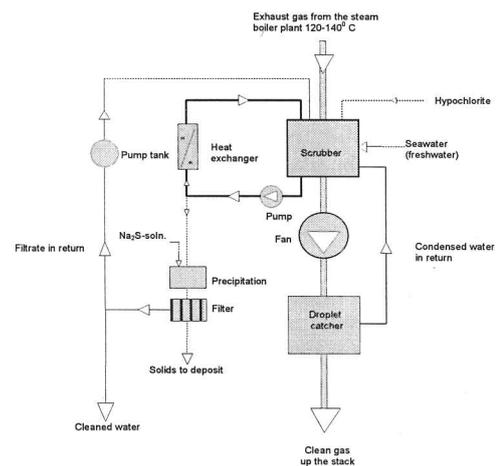
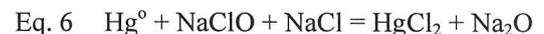
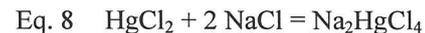
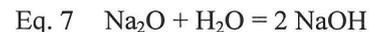


Figure 6 The MILTEC process

1. The gas is washed with seawater added a 15 % sodium hypochlorite (NaClO) solution. By keeping the red/ox potential and the pH at a given level, water-soluble HgCl₂ is formed by the following equations:



Other side reactions can be:



Na₂HgCl₄ is a stable water-soluble complex, easily absorbed by seawater. If the red/ox potential is too low, the less soluble salt Hg₂Cl₂ is formed. This product is the end product in other Hg-cleaning operations. The precipitation of this salt often results in clogging in valves and piping. By keeping the

red/ox potential and the pH at controlled levels this may avoided.

In addition, the water collects the dust, and the SO₂-gas is oxidized to sulphuric-acid. This prevents the reduction of Hg⁺⁺ ions to Hg⁰-gas by the SO₂-gas.

2. The gas and the wash water are let co-currently through a fixed bed of lumpy limestone. The bed acts as a powerful turbulent mixer for the gas and the water. In addition, the sulphuric acid is converted to gypsum (CaSO₄); keeping the pH constant around 5-6. By adding enough seawater, the produced gypsum will not attach to the lumpy limestone, but follow the wash water.

3. The washed gas and wash water hit the surface of the underlying wash water tank. The gas, which is now cleaned, is sucked off, and is continuously let out over the roof. The water now containing mercurysalts; dust and gypsum are absorbed in the reservoir tank.

4. The water is periodically pumped from the reservoir into 2 precipitation tanks, where disodiumsulfide (Na₂S) is added. This leads to the formation of mercury-sulphide (HgS) and other metal sulphides precipitate. HgS precipitates after the following equation:



5. The water from the precipitation tanks is filtered, producing a filter cake with the following analysis:

Hg	1,7 %	Mo*	55
As	,12 %	Na	1,1 %
Ba	242	Ni	381
Cd*	335	P	508
Co*	50	Pb*	414
Cr	671	S	8,5 %
Cu	95	Sr	193
K	0,4 %	Zn*	0,25 %

Table 1 Example filter-cake analysis. (Analysed by Rødmyr Miljøsenster, Skien, Norway)

All analysis in ppm unless otherwise stated. *Analysed by ICP-MS, others by ICP-AES.

Due to the amount of Sulphur, it can be concluded that Hg is in the form of HgS. This

is confirmed by SEM-analysis⁷ (Scanning Electron Microscope).

The filter cake can be deposited on a land fill deposit for special waste, NOAH (Norsk Avfallshåndtering AS), Langøya. The filtrate, which contains <0,5 µg/l mercury, is returned to the gas-scrubbers in the primary off-gas cleaning system.

3.6.2 EXPERIENCE AND RESULTS FROM OPERATION

The operation started up April 3rd 2000. From then on, and to late December, the cleaning plant has gone through a "fine tuning" phase and most of the occurring problems were solved during the summer and autumn. From late august to mid November the Hg-cleaning facility was out of operation due to a revision/maintenance stop at the thermal power plant. During this period several changes were done. Some of them are mentioned in the following text.

The first Hg measurements showed values as low as 1-5 µg Hg/Nm³. However, it was discovered that these values were on the low side. The Hg analyser, a "Semtech Hg 2000", was only able to analyse Hg⁰. Hg in ionic form, dissolved in water, was not detected. Bubbling the gas through an ascorbic acid solution (vitamin C) solved this problem. Doing so, the Hg-ions are reduced to Hg⁰. The normal level after cleaning is now 5-10 µg Hg/Nm³ for the dry gas. The results with the reduced ions are somewhat higher. The origin of these Hg ions is water droplets that have been drawn off by the fan, which suck the gas through the plant.

In order to minimise the amount of water mist in the off-gas, a droplet catcher has been installed after the fan and a heat exchanger (cooler) was installed to cool the wash water. In addition the chimney height has been increased from 15 to 42 m.

Clogging of the outlet pipe when adding sodium hypochlorite to the wash water also caused some problems. Cutting the outlet pipe above the wash water level easily solved this problem.

By increasing the chimney height, a new problem occurred. The water mist of the off-gas condensed inside the chimney, resulting in relatively large amounts of condensed water

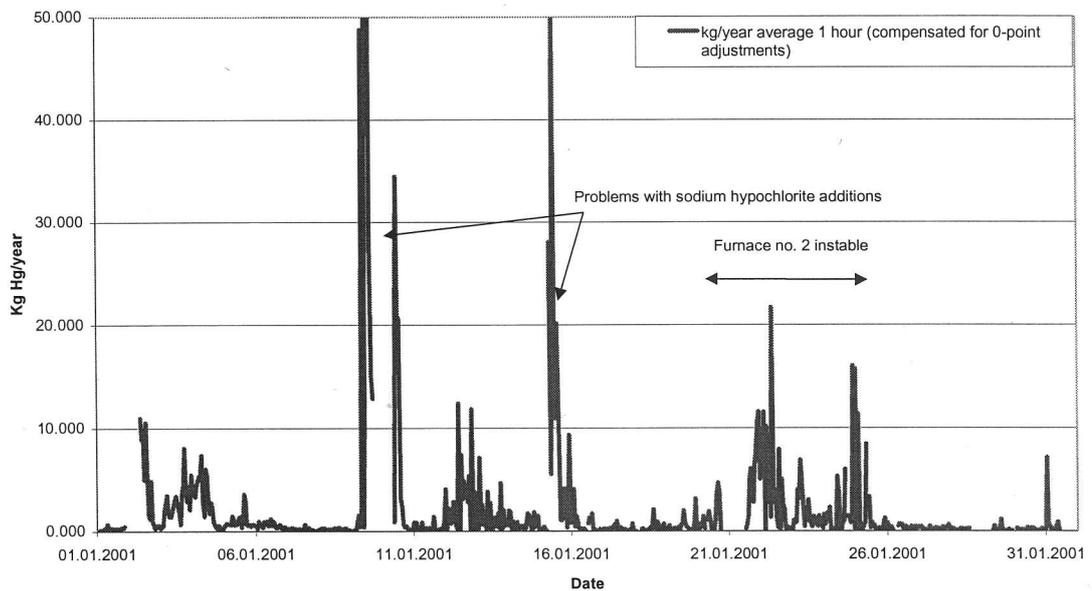
moving up and down. However a new design of the chimney outlet will solve this problem. Freshwater has also been tried for the washing of the gas with similar good results. So far this has been done only once. Only seawater is being used at the moment. The Hg analyser, a "Semtech Hg 2000", is very well suited to measure the Hg⁰-content of the gas.

The process removes mercury, but also other heavy metals and compounds will be removed

from the off-gas, see table 1. The emission of dust is also reduced.

The operational result in Figure 7 shows that the cleaning facility is running well and that the emissions are sufficiently low. Although some "fine tuning" remains, it is felt that the Hg-removal installation is working as expected.

Hg-emissions after the cleaning facility, 1. january - 31. January 2001



4. CONCLUSIONS

Tinfos has, since the findings of Mercury in the off-gas system in 1993 worked to find a solution to the emission problem. The signals from the national authorities and from the EU have been a major driving force during this work.

Several existing technologies have been considered. However, none of these were able to meet the demands from SFT of some 15 kg Hg/year. Therefore, Tinfos looked for alternatives. Together with Miltec, a new technology for the removal of mercury was developed. This technology may be used on a various type of plants (ferroalloy, waste to power, crematories etc.).

Based on the experience of 6 months of operation to date, the cleaning plant have the following features: an off-gas with 5-10µg

Hg/Nm³ is obtained, this represents a > 90 % reduction of emissions and is below the demands set by the authorities. The filtrate contains <0,5 µg/l mercury, and can be returned to the primary gas-cleaning circuit. The sludge contains approx. 1.7 % Hg as HgS. It can be concluded that the plant so far is able to meet the demands from SFT regarding mercury, in addition the emissions of other heavy metals and dust are reduced. This is obtained in a plant with both low investment- and operational costs.

5. Acknowledgements

The authors wish to thank employees at Tinfos for fruitful discussions during the work with this paper.

Figure 7 Hg-emissions to air after cleaning facility.

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