# STUDY ON APPLICATION OF MOLTEN SALT OXIDATION TECHNOLOGY (MSO) FOR PVC WASTES TREATMENT

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*ABSTRACT:* The project:" Study on application of molten salt oxidation (MSO) for PVC plastic wastes treatment" should aim three followings: 1) Installation of lab-scale MSO unit with essential compositions builds up foundation for the 2) estimation of waste destruction efficiency of the technology. 3) Based on the results of testing PVC - the chlorinated organic wastes on the lab-scale unit, the ability of the technology application at pilot-scale level will be primary estimated.

The adjustment and correction of some compositions in the lab-scale unit theoretically designed during experiment overcame the shortages by design and fabrication such as heat distribution regime, feeding wastes and draining spent salt. These solutions adapt to the technical requirement of operation as well as scientific requirement of the research on MSO process.

PVC waste treatment was tested on the MSO lab-scale unit in different conditions of operation temperature, superficial air velocity related to air/oxygen feeding rate, waste feeding rate. The testing results showed that destruction efficiency of chlorine in MSO technology was almost absolute. HCl and $Cl_2$ emission were insignificant in different operation conditions. HCl and $Cl_2$ emission depend on resident time and nature of molten salt. However, with inherent attributes of MSO technology emission of CO is not avoided in processing waste treatment. Therefore, finding active solutions for reduction CO emission is essential to complete the technology.

The experiments also were carried in conditions of single molten salt ($Na_2CO_3$) and molten ($Na_2CO_3$ – $K_2CO_3$) eutectic. The comparison of efficiency of these tests gives idea of using molten salt eutectic to reduce operation cost in MSO technology.

Based on operation parameters and scientific verification results during experiments, the introductory procedure of waste treatment by MSO process was built up. Thereby, primary estimation of development of the technology in pilot-scale is given.

## INTRODUCTION

With convincing results of tests on MSO unit for treatment of several varieties of hazardous wastes in the many laboratories on the world, molten salt oxidation technology has been considered as a best demonstrated available technology (BDAT) [1]. The technology also is affirmed as an environmental friendly technology for hazardous wastes treatment. With above meaning, project:" Study on application of molten salt oxidation technology (MSO) for PVC plastic waste treatment " is taken the initiative for the goals: (1) verifying efficiency of MSO technology for treatment of hazardous wastes, especially, high pollutant potential wastes such as chlorinated organic; (2) estimating technical and economic ability to satisfy special requirement of the technology.

The project needs to carry out three following investigations:

- Installation and correction the MSO lab-scale unit with capacity of 0.3-0.5kg/h.
- Investigation of treatment efficiency for PVC wastes, testing on the MSO lab-scale unit.
- Establishment of introductive procedure of waste treatment on the MSO unit.

In 2004 year the design of MSO lab-scale unit with capacity of 0.3-0.5kg/h was made. Based on this design, in 2005 year the MSO unit with essential compositions is installed and corrected for foundation of studying technology.

The second study is most important content of the project. This is to verify absolutely efficiency for treatment of problematic wastes such as PVC by MSO process. PVC containing high concentration of chlorine (46-52%) that always is considered as the difficult wastes for treatment by conventional solution such as incinerator. Therefore results of testing PVC on MSO unit are provable convincingly advantages of the technology for treatment of hazardous wastes.

This paper presents the summary of study contents in the Project.

## STUDY CONTENTS

### Installation and correction of MSO lab-scale unit with 0.3-0.5 kg/h capacity

The MSO lab-scale unit with 0.3-0.5kg/h capacity is installed and corrected for the following compositions (see appendix):

*The reactor vessel and waste feeding unit.*

The destruction of wastes by molten salt oxidation processes in the reactor. The reactor is a vessel of 1meter tall and 110mm inside diameter over the top part and 78mm inside diameter over the bottom part, with 350mm long, tapered transition zone in between. The vessel is fabricated from 10mm thick alloy of 20% nickel material. The vessel is held from the top and mounts on a roof sheet of the heater unit that covers the reactor. The vessel also has a salt drainpipe extending from the bottom of the vessel to outside of the heat zone.

The air and wastes enter reactor through an injector lance extending through the vessel cover to the bottom of vessel. The injector is double-pipe with 40mm inside diameter of outer pipe and 22mm inside diameter of inner pipe. Wastes through inner pipe to bottom of the reactor always are kept at low temperature until leave the injector and contact with molten salt. Compressed air is supplied to both outer and inner pipe for cooling wastes and introducing wastes to the bottom of the reactor.

*The heater unit and temperature controller*

The heater unit, radiant electric type, is used to melt the salt in the reactor vessel.. The heater unit is made up three subassemblies covering three zones of reactor, which is capable of heating the vessel to maximum temperature of 1200ºC. The annular gap between the heaters and the vessel is covered with 20cm thick heat–resistant material to keep the heat from escaping due to induced natural convection.

The heater unit is connected to main power supply via the temperature controller unit. The temperature controller unit includes three K-type thermocouple reading temperature up to 1200ºC. These thermocouples are placed touching the outside of the reactor at different height, respecting to three heat zones. These three thermocouples

show the temperature on the outer surface of the reactor at each heat zone. All the three heat zones at different height are controlled individually by the three digital controllers. The controllers read the temperature through the three corresponding thermocouples and control the current sent to the heaters by relays.

*The off-gas treatment unit*

The off-gas treatment unit has two functions: (1) reducing temperature of off-gas released from the reactor and; (2) removing very small particles present in off-gas. The unit includes a heat-exchange equipment and a HEPA filter. The heat-exchange that operates according to water-air indirectly exchange method reduces temperature of off-gas from 313$^o$C to <50$^o$c. The HEPA filter keeps particles more than 0.3μm with efficiency up to 99,97%.

*The draining spent salt assistant unit*

Since the drainpipe that is outside of heaters is not heated during operation, the salt here always solidifies and forms solid plug in the pipe. To drain spent salt became solid the drainpipe needs to heat. A tool using mainly a torch assists to drain spent salt. The torch connected to gas burner supplement equipment heats drainpipe up to high temperature (>melting point). Melt salt flows out through the pipe into the crucible below.

**Investigation of treatment efficiency for PVC wastes**

PVC (polyvinyl chloride) is a kind of polymer. PVC is made by chemically linking together many monomers – vinyl chloride ($C_2H_3Cl$). PVC contains high chlorine constituent up to 46-52%. Therefore PVC wastes are considered as difficult wastes for treatment by incineration solution. A comprehensive study by the American Society of Mechanical Engineers (1995) found correlation between the presence of PVC wastes and dioxin emission in more than 1,900 incineration test, conducted at solid and hazardous waste facilities around the world [2]. Any burning chlorine containing organic material gives rise to the production of dioxin and hydrogen chlorine HCl. There is always HCl released firstly in processing PVC in incinerator. Then contact between HCl and hydrocarbon subsequently formed can produce chlorinated organic, the precursors of dioxin and furan. [3]. Therefore HCl or chlorine containing compounds need to limit to minimum in processing hazardous wastes. For estimation of destruction efficiency of MSO technology, investigation of HCl and free chlorine ($Cl_2$) emission in MSO process is essential. In addition, for processing organic waste estimation of combustion efficiency is determined by carbon monoxide CO and carbon dioxide $CO_2$ emission. The higher the amount of carbon dioxide and the less the amount of carbon monoxide, the higher will be the combustion efficiency [4]. Therefore investigation of CO emission from MSO process is important second content in the framework of the project.

***Experiments in single molten salt condition***

**Experimental procedure**

The main mechanism of oxidation in MSO process is bubble involved oxygen transfer rate (OTR) from gas phase to liquid phase. Based on analysis of effect on OTR in bubble, the factors are determined to investigate their influences on oxidation efficiency in MSO process. The factors are bases to set experimental conditions for investigation of destruction efficiency in MSO technology. In addition experimental

results in foreign reports about MSO technology research also are basis for setting experimental conditions. The experiments are carried in different conditions of height of melt salt, operation temperature in three heat zones, superficial air velocity related to oxidizing air feed rate and waste feed rate affecting resident time.

- The height of melt salt is chosen with ratio between length and diameter (L/D) of the reaction zone of 2-3. The amount of salt filling into reactor is determined by specific weight of molten salt and volume of salt occupying at calculated height of melt in the vessel.

- Operation temperatures in three zones are changed of 720 – 750 at top and 870- 1000$^{o}$C at center and bottom zone of reactor.

- Superficial air velocity is changed by different air supply rate. Superficial air velocity ($V_s$) is chosen with varieties >0.15m/s.

- Waste feed rate depends on amount of wastes fed and time for feeding. The feeding waste is batch feed.

To estimate exactly influence of the above factors some tests run on the MSO unit without gaseous filter in off-gas treatment unit. Thereby it is given estimation of effect of HEPA filter on secondary waste emission. The tests of PVC wastes run on the MSO lab-scale unit in 10 condition groups (see APPENDIX- Table 1).

Every experiment was carried out on MSO unit with filled into reactor $Na_2CO_3$ salt of calculated amount. PVC medical transition tubes after determined physical and chemical characteristic by proximate analysis and X-ray fluorescent analysis (see APPENDIX-Table 2 and Table 3) were cut less than 5mm size for fuel fed into the reactor. After operation temperature reached to target set on the controller unit before heating reactor, fuels were fed through feeding waste unit. Amount of fuels and time for feeding were recorded to calculate waste feed rate. Off-gas treatment unit started to operate after feeding waste in 5 minutes. During operation tests of HCl and CO emission were implemented mainly by Gastec detector tubes with standard deviation of about ±10-15%. It is confirmed that the results of experiments just give primary investigation because of deviation in measurement and not much data.

**Result and discussions**

The results of measurement of HCl, $Cl_2$ and CO concentration in off-gas (shown in Table 4-APPENDIX) are basements for following discussions.

***HCl and $Cl_2$ emission***

In general, hydrogen chlorine and free chlorine emissions were insignificant in all experiments on MSO lab-scale unit. HCl concentration just is detected in condition of melt salt height at L/D ratio fixed be <3 with maximum figure not exceed 10ppm. The predication for formation HCl from the incineration of chlorinated organic material makes HCl dominates in off-gas released from incinerators. The absolute destruction efficiency of halogen is most important feature of MSO technology. One prediction that by using strong alkaline salt such sodium in MSO process, substantial HCl is immediately completely neutralized in large active sodium environment to convert inorganic captured in molten salt [5]. It also is able to propose that there is a dominating surface reaction of direct absorption of the fuel-bound chlorine by the salt in MSO reactor, which might be taken place at the bubble surface where plenty of active sodium [5].

- ***CO emission***

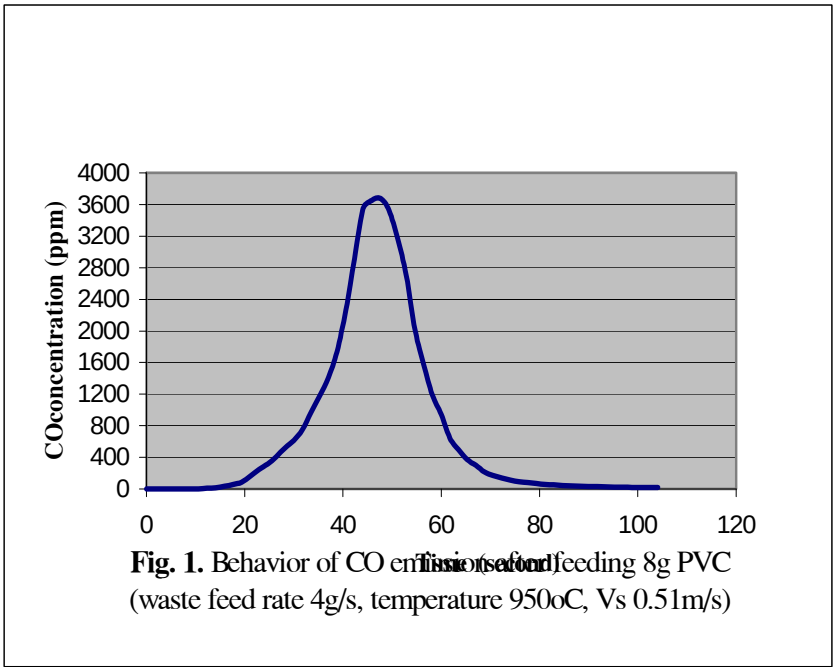


**Fig. 1.** Behavior of CO emission (second) feeding 8g PVC (waste feed rate 4g/s, temperature 950oC, Vs 0.51m/s)

Chlorine containing compound and chlorine were not observed in tests while CO emission was considerable. Figure 1 illustrates behavior of CO emission from MSO reactor through the measurement of variation of CO concentration in off-gas with time by Testo 335 equipment. This could be explain that with 91% volatile matters, large amount of hydrocarbon is firstly released just at 50$^{th}$ second after feeding waste into reactor. This prompt release causes extremely high CO emission [3]. The results show influence of temperature on CO emission. CO emission reduces with increasing of temperature. The observation of variation of CO concentration depending on temperature is shown in figure 2. The complete reaction in thermal-oxidation process depend on three factors 3 T – temperature, resident time and turbulence. In MSO process, turbulence level is determined by superficial air velocity Vs also being function of air volume or air feed rate. Efficiency of the process increases with increase of Vs due to turbulence increases. However, the experimental results in study of hydrodynamics in MSO reactor show that strong effect of Vs on efficiency of process just is less than 0.15m/s [6]. An observation here of effect of Vs>0.15m/s on combustion efficiency for CO seems to be agreement with that in figure 3. In addition to the above observation, with high superficial air velocity up to 0.51m/s, salt is detected in off –gas exhaust system because of entrained salt. Superficial air velocity is function of supplied air volume. The study of bubble mechanism shows that supplied air volume related directly proportionately to diameter of bubble affects resident time in process. Resident time increases with reduction of diameter of bubble[5]. This also can give the comment that supplied air volume needs to consider in MSO process.

The influence of filter on the CO emission is considerable. Emission of CO reduces from 500ppm at experiment T7 without filter to 350ppm at experiment T1 with loading filter.

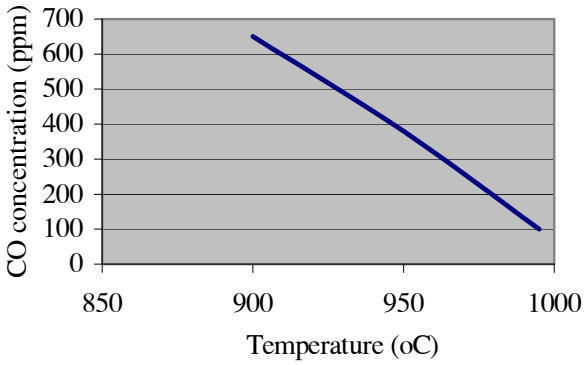


**Fig. 2.** The influence of temperature on CO emission (waste feed rate 3g/s, Vs 0.31m/s)

***Feeding wastes and back propagation.***

With specific mechanism operation, feeding waste is a problem in MSO technology. Since wastes were fed from top of reactor there is always volatilization of waste due to the fuels contact with high temperature at reactor top. Especially, for PVC with large volatile back propagation in experiments is very difficult to feed wastes. Some known factors able to prevent back propagation are cooling injector and creating negative pressure in reactor. For latter one, creation of negative pressure in reactor involves high enough off-gas exhaust to overcome surely positive pressure resulting from high temperature and supplying oxidizing air in reactor. This, however, is conflict with requirement of minimization off-gas volume to reduce emission of substantial material. Therefore solutions not only for prevention back propagation but also for reduction of secondary waste emission need to consider for optimum procedure to satisfy requirement of treatment efficiency and operation.

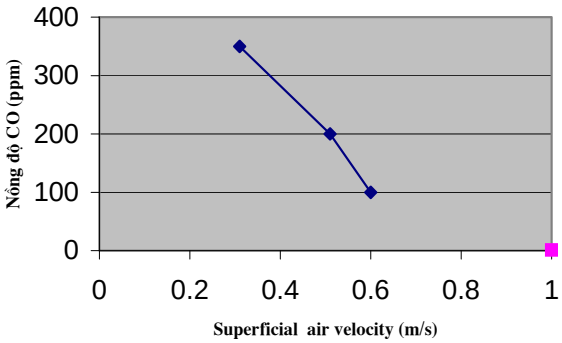


**Fig. 3.** The influence of superficial air velocity on CO emission(waste feed rate 2g/s, temp. 870oC)

***Experiments in molten slat eutectic condition.***

*Experimental conditions*

In awareness that the melting point of molten slat eutectic being lower than that of single molten salt and therefore it can be reduced operation cost in MSO technology. For this reason investigation of destruction efficiency in molten slat eutectic can give idea of reduction operation cost in processing wastes by MSO technology.

Molten $Na_2CO_3$-$K_2CO_3$ eutectic with 56/44 ratio was used for investigation HCl and CO emission from MSO reactor. The choice molten Na-K carbonate eutectic for MSO process is due to this eutectic is stable and, furthermore, it favors to form peroxide species for catalytic converting wastes [7]. The experiments were implemented in 6 different condition groups of temperature (800-870$^o$C), superficial air velocity (0.26-0.31m/s) and waste feed rate (0.2-2.5g/s).

All experiments carried out in condition of melt salt height of 23cm and without HEPA filter. In this study, the influence of amount oxidizing air on CO emission was observed through estimation of fuel-air mixture level affecting oxidation of carbon. An equivalent ration $\phi$ is given to estimate actual fuel-air mixture ration compared to stoichiometric fuel-air mixture ratio. Factor $\phi$ is determined following equation [5]:

$$\phi = \frac{(g_{fuel} / g_{air})_{stoi.}}{(g_{fuel} / g_{air})_{act.}}$$

Here, stoichiometric fuel-air mixture ratio is determined by following equation:

$$C_2H_3Cl + 0{,}5Na_2CO_3 + 2{,}5\ (O_2 + 3{,}76N_2) = 2{,}5CO_2 + 1{,}5H_2O + 9{,}4N_2 + NaCl.$$

Actual fuel-air mixture ration is determined by waste feed rate and air feed rate for processing. Amount of waste with feed rate of 0.2g/s was introduced together amount of oxidizing air with feed rate order of 4.3m$^3$/h (1.43g/s) and 5.1m$^3$/h.(1.7g/s) In these conditions the equivalent rations $\phi$ are 1.5 and 2, respectively.

*Results and discussions*

Like in condition of molten $Na_2CO_3$ salt, HCl and $Cl_2$ concentration in off-gas are not detected in molten $Na_2CO_3$-$K_2CO_3$ eutectic although operation temperature is lower than. This is provable that chlorine destruction efficiency just depends on resident time related to height of melt and nature of the molten salt.

In an investigation, with increasing equivalent ratio of 1.5 and 2 concentration of CO in off-gas reduced to 50-30ppm. Though data of these experiments are not much it can be proposed that emission of CO reduced considerably due to mixture between wastes and oxidizing air is much higher.

**CONCLUSION**

Investigations of waste treatment for chlorinated organic such as PVC plastic on the MSO lab-scale unit with 0.3-0.5kg/h capacity prove that absolute chlorine destruction efficiency is most important feature of MSO technology. In addition MSO technology has many advantages. Structure of the technology equipment is relatively simple. Therefore the operation and the maintenance of MSO unit are relatively easy. Operation parameters also show energy supplied in the processing wastes is not much. Inasmuch as PVC plastic is energetic material, the oxidation of the wastes supplies some heat, thereby reducing electric power to maintain the high temperature.

With some inherent characteristics about limited resident time and low operation temperature emission of carbon monoxide can not be avoided. To reduce CO emission it needs to find out the active solutions for enhancement complete oxidation reaction of carbon. The solutions can be either enrichment of oxygen or addition catalyst oxide materials in process. The problem of feeding waste can be solved by technical methods such as increase of cooling effect of injector, installation of reasonable waste feed system and creation of negative pressure in reactor.

The material that can resist high corrosion in reaction media with salt at high temperature is an attentive especial problem of the MSO unit.

In limited framework of project about duration and budget, scientific analytic result for molten salt oxidation technology is still restricted. However, by the experimental results it can be confirmed that oxidation molten salt technology has potential ability to application at higher than laboratory scale, pilot-scale, for treatment of chlorinated organic wastes.

**ACKNOWLEDGEMENTS**

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**Tab 1.** The condition groups for testing PVC wastes

| No | Symbol | Height of melt salt (cm) | Operation temperature (°C) | | | Superficial Velocity (m/s) | Waste feed rate (g/s) | Note |
|---|---|---|---|---|---|---|---|---|
| | | | Top zone | Center zone | Bottom zone | | | |
| 1. | T1 | 18 | 754 | 900 | 871 | 0.31 | 3.0 | loading filter |
| 2. | T2 | 18 | 751 | 900 | 871 | 0.51 | 3.0 | loading filter |
| 3. | T3 | 18 | 753 | 900 | 870 | 0.6 | 3.0 | loading filter |
| 4. | T4 | 26 | 776 | 970 | 900 | 0.31 | 3.0 | new filter |
| 5. | T5 | 26 | 776 | 900 | 900 | 0.51 | 3.0 | loading filter |
| 6. | T6 | 26 | 720 | 900 | 900 | 0.31 | 3.4 | no filter |
| 7. | T7 | 26 | 720 | 900 | 900 | 0.31 | 3.0 | no filter |
| 8. | T8 | 26 | 900 | 975 | 900 | 0.31 | 3.0 | no filter |
| 9. | T9 | 26 | 900 | 970 | 950 | 0.51 | 2.5 | no filter |
| 10. | T10 | 26 | 900 | 995 | 900 | 0.31 | 3.0 | no filter |

**Tab 2.** Result of proximate analysis of tested PVC wastes

| **Moisture** (wt. %) | **Volatile matter** (wt. %) | **Ash** (wt. %) | **Fixed carbon** (wt.%) |
|---|---|---|---|
| 0.2 | 91 | 1.0 | 7.8 |

**APPENDIX**

**Tab 3.** Results of constituent analysis of tested PVC wastes

| **Elements** | **Pick area (cps) and standard deviation** |
|---|---|
| Cl | 1878.071 (± 5.220) |
| Ca | 307.131 (± 2.275) |
| Ti | 34.531 (± 0.821) |
| Cr | 22.179 (± 0.724) |
| Fe | 108.675 (± 1.365) |
| Pb | 619.162 (± 3.142) |

**Tab 4.** The results of measurement of HCl, $CL_2$ and CO concentration in off-gas

| **Conditions** | **HCl concentration** (ppm) | **$Cl_2$ concentration** (ppm) | **CO concentration** (ppm) | **Note** |
|---|---|---|---|---|
| T1 | 1,5 | no detected | 350 | loading filter |
| T2 | 10<br>8 | no detected | 200 | loading filter |
| T3 | 0,7 | no detected | 100 | salt entrained |
| T4 | no detected | no detected | 600<br>350<br>20 | Measuring CO in 2 minutes after feeding 12gPVC, new filter |
| T5 | no detected | no detected | 400<br>150<br>9 | Measuring CO in 2 minutes after feeding 12gPVC, loading fil. |
| T6 | no detected | no detected | 800<br>500 | Measuring CO in 2 minutes after feeding 15gPVC, no filter. |
| T7 | no detected | no detected | 500<br>40 | Measuring CO in 2 minutes after feeding 12gPVC, no filter. |
| T8 | no detected | no detected | 400 | no filter |
| T9 | no detected | no detected | 300 | no filter |
| T10 | no detected | no detected | 100 | no filter |

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