

The kinetics of activation and deactivation in the process of water ozonising used for advanced oxidation of the dust waste from moulding sands

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Abstract

Adding coal dust and organic carriers of the lustrous carbon to bentonite-bonded moulding sands in amounts justified by the technological regime and the use of cores and protective coatings based on organic compounds create serious threats to the environment. During thermal destruction of the individual components of moulding and core sands, some toxic organic compounds are emitted. They form the majority of the Hazardous Air Pollutants (HAPs), and include mainly compounds like benzene, toluene, xylene, naphthalene, hexane, acetaldehyde, acrolein, aniline, cresol and cumene, their polycyclic derivatives, phenol, formaldehyde, and other similar matters. In thus formed dust waste, the amount of which constitutes about 20% of all the waste from foundries using traditional moulding and core sands, there are still full-value materials which can undergo total recycling, providing the HAPs are partially or totally removed from them. The article discusses some problems of the advanced oxidation of selected toxic chemical compounds present in bentonite-bonded moulding sands due to the effect of high temperature. The results of the investigations of the kinetics of the process of maximum water saturation with ozone (acting as an oxidiser) and of the kinetics of the natural process of ozone decomposition to diatomic oxygen were presented. It has been stated that the maximum time of water saturation with ozone using an OZOMATIC OSC-MODULAR 4HC ozone generator and a 1m³ capacity tank with water is 60 minutes. After 30 minute break in the ozonising process, the ozone concentration in water decreases by 40 to 50%. To obtain maximum ozone concentration in water during the next ozonising cycle, it is necessary to have the ozone-generating device running for the next 30 minutes. The stabilisation of ozone concentration in water takes place only after the third ozonising cycle, when it reaches nearly 80% of the maximum value obtained after the first process cycle

Keywords: bentonite sands, toxic compounds, advanced oxidation, ozone, kinetics of dissolution

1. Introduction

Problems related with advanced oxidation (AO) of selected chemical compounds to neutralise their adverse effect have been the subject of numerous studies, not always included in the field of foundry practice. The main issues to investigate included the kinetics of the oxidising reaction and the resulting products

formed in potable water [1-3] as well as the oxidising process of benzene [4,5] and phenols [6]. The increasing pressures put by ecology and economy force foundries all over the world to look for more profitable production means and reduce to minimum the harmful waste in both gaseous and solid form. At the close of the 90ties of the past century, the technical literature mentioned for the first time the application of AO process in foundry industry [6-15]. The, commonly used in moulding sands, additions of coal

dust, organic carriers of lustrous carbon, and phenolic, urethane and other organic binders for core sands are the main source of air pollution. Yet, reducing the amount of these additives makes casting quality deteriorate quite considerably. Advanced oxidation process (AOP) is generally defined as a process of oxidation taking place in the aqueous phase and consisting in the formation of hydroxide radicals or other intermediate products of reaction, which in the course of the oxidising processes make the transformation and/or decomposition of certain contaminants possible. The AO process can use various techniques (chemical, photochemical, sonochemical, radiation), or their combinations, the main goal of all of them being the chemical decomposition and destruction of contaminants.

The AOP offers a solution to the high level of harmful and toxic emissions. Under certain conditions, during advanced oxidation, a large amount of carbon can be transformed into active products, which next serve as adsorbents of Volatile Organic Compounds (VOC) and Hazardous Air Pollutants (HAPs). Additionally, the substances used in AO may enter into reaction and cause degradation of some organic compounds present in common moulding sands. Depending on conditions (the amount of oxidiser and the pH values) under which the respective reactions are taking place, the decomposition of organic pollutants in the process of oxidation is proceeding according to different mechanisms, which include direct oxidising, indirect oxidising and direct photolysis. For example, when the oxidisers are molecular ozone and hydrogen peroxide, the indirect product may be formed as a result of ozone and hydrogen peroxide getting combined together; these radicals, in turn, may get engaged in the reactions of both oxidising and reduction. The, formed in the AO process, radicals usually become very reactive at high temperatures, commonly present in traditional moulding sands when they get in contact with molten metal. Theoretically, following the rule of addition or absorption, it is possible for the radicals to get combined with pollutants like benzene, toluene and phenol. Due to the effect of these mechanisms, the VOC may undergo partial decomposition. Sometimes the AOP mechanism consists in changing the adsorption power of bentonite and other constituents of common moulding sands, thus improving their adhesion behaviour.

2. Water activation with ozone and the obtained results of investigations

The process of advanced oxidation by ultrasonic effects is carried out in ozone-saturated water; the proper environment is produced by an *OZOMATIC OSC-MODULAR 4HC* ozone-generating device, fed with oxygen (Fig.1). Ozone is delivered through an injection nozzle to water in a closed system; the tank capacity is 1m³. Nominal rate of ozone generation in a device of this type is 4g/Nm³. Ozone in concentrations used by industry is a colourless gas, unstable and decomposing at room temperature to diatomic oxygen. The process of its decomposition is accelerated through contact with the solid surfaces, chemical compounds, and high-temperature environment. The heat of ozone formation is 144,7 kJ/mole, and its solubility in water at 20°C is 3 ppm. In view of these characteristics, it is necessary to determine maximum concentration of ozone in water as well as the kinetics of its decomposition under real conditions. All these investigations were carried out under different configurations shown in Figure 2. They enable using water saturated with ozone in a proper concentration.

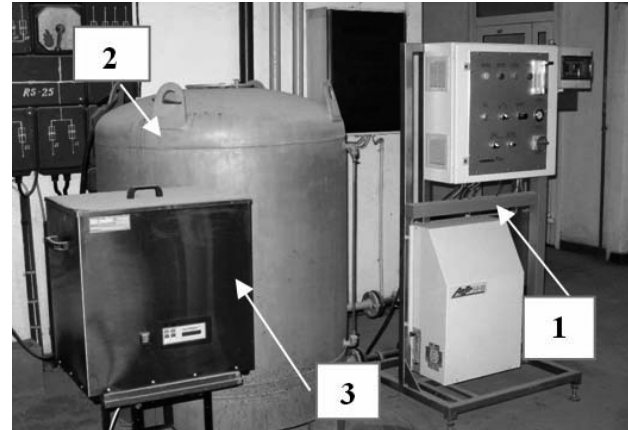


Fig. 1. Pilot stand for water saturation with ozone and for ultrasonic processing of dust waste from moulding sands (1 – Ozomatic OCS Modular 4HC ozone generator, 2 – compensation tank, 3 – ultrasonic chamber)

Physico-chemical examinations conducted by standard research methods (Table 1) and by FTIR spectroscopy on Excalibur 3000 spectroscope with standard DTGS detector (Fig.3) have confirmed the decay of ozone-saturated water activity after the time longer than 210 minutes. This is proved by the same values of the wave number in IR spectra and of the hypermanganate index, i.e. oxygen consumption ($< 0,7 \pm 0,1$), obtained for water non-ozonised and subjected to the ozonising process for 60 minutes. It should be observed, however, that the process of water ozonising also causes permanent changes in some physico-chemical properties of water (Table 1). Ozonising of water raises its alkalinity, electrolytic conductivity, overall hardness and iron content, while reducing quite considerably the content of ammonia, chlorides and nitrates.

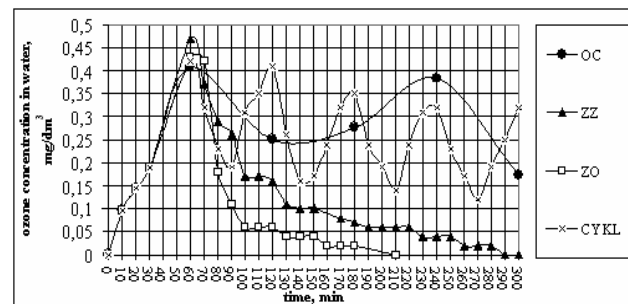


Fig. 2. Kinetics of water activation with ozone and deactivation. Designations on the graph: OC – change of ozone concentration in 1000 dm³ water volume during continuous operation of ozone generator, ZZ – change of ozone concentration in 1000 dm³ water volume in closed tank after 60 minute operation of ozone generator followed by switching the device off, ZO – change of ozone concentration in water fed to an open 30 dm³ capacity tank after 60 minute ozone generating cycle, CYKL – change of ozone concentration in 1000 dm³ water volume due to intermittent operation of ozone generator in cycles: 60 minute ozonising – 30 minute break – 30 minute ozonising resumed (total operating cycle – 300 minutes)

Table 1
Effect of water ozonising on physico-chemical properties

physico-chemical properties	non-ozonised water	ozonised water	change in respect of non-ozonised water %
pH	7,65	8,30	+ 8,5
electrolytic conductivity, $\mu\text{S}/\text{cm}$	317	319	+ 0,6
overall hardness, mgCaCO_3/l	148	153	+ 3,4
Fe, mg/l	0,067	0,076	+ 13,4
Mn, mg/l	< 0,025	< 0,025	0
ammonia, mg/l	0,035	< 0,015	- 57,1
chlorides, mg/l	27,3	14,9	- 45,4
nitrites, mg/l	< 0,01	< 0,01	0
nitrates, mg/l	11,3	6,8	- 39,8

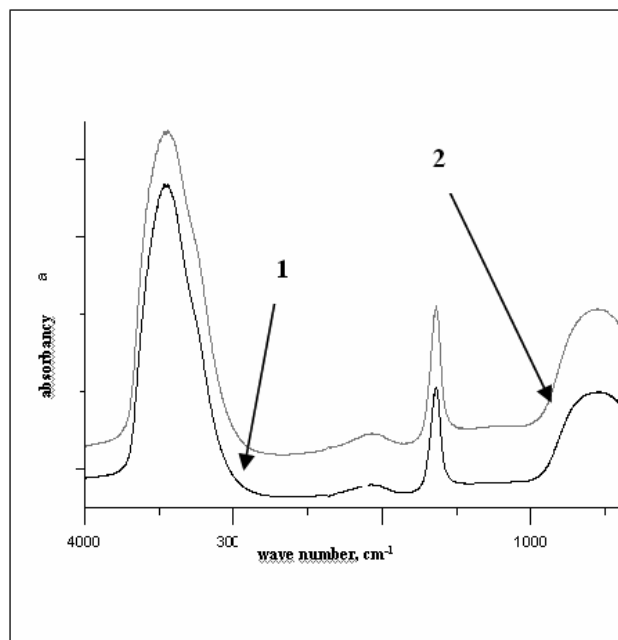


Fig. 3. FTIR spectra for nonozonizing water (1) and water ozonizing by 60 minutes (2), after the time decay longer than 210 minutes

3. Conclusions from the investigations

1. Continuous operation of ozone generating device results in maximum ozone concentration in water after the ozonising time of 60 minutes.
2. The time of continuous ozonising prolonged to 120, 180, 240 and 300 minutes reduces ozone concentration in water, which (respective of the maximum concentration obtained after ozonising for 60 minutes) now amounts to 55%, 60%, 90% and 40%. For this reason, in thus conducted process of water ozonising, obtaining the stable ozone concentration values is not possible.

3. Periodical operation of ozone generating device consists in obtaining maximum ozone concentration in water after 60 minutes, followed by 30 minute break in the process and its reactivation for 30 minutes after each next break. Applying these cycles of ozonising, ozone concentration in water was observed to drop by 40 to 50% after a 30 minute break in operation of the ozone-generating device. To obtain maximum ozone concentration in water during the next ozonising cycle, it is necessary to have the ozone-generating device running for the next 30 minutes. The stabilisation of ozone concentration in water takes place only after the third ozonising cycle, when it reaches nearly 80% of the maximum value obtained after the first process cycle.

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