

# RESEARCHES ON THE USE OF OXYGEN CONCENTRATORS IN WASTEWATER OXYGENATION

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**Abstract** - The paper presents a solution for increasing the dissolved oxygen content in the water by the adsorption of N<sub>2</sub>, CO<sub>2</sub>, etc. with the help of absorbents called zeolites; the equation of oxygen transfer rate to water is numerical integrated. The construction solution and the technical characteristics of an oxygen concentrator to be used in experimental researches are described. The experimental installation comprises modern instruments for measuring the gas flow rate, the pressure, the temperature and an oxygen meter. At the end of the paper the results of the theoretical and experimental researches regarding the increase of dissolved oxygen content in water are presented.

**Keywords:** Oxygen Concentrators, Water Oxygenation, Oxygen Meter, Oxygen Dissolved in Water.

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## 1. Introduction

To increase the dissolved oxygen concentration in water there are several versions of introducing gases into water as [1]:

I) The introduction of pure air of 21% O<sub>2</sub> and 79% N<sub>2</sub> (volumetric ratio);

II) The introduction of a gaseous mixture of atmospheric air and gaseous oxygen from a cylinder in certain proportions;

III) The introduction of air with low nitrogen content (95% O<sub>2</sub> and 5% N<sub>2</sub>) supplied by oxygen concentrators;

IV) The introduction of ozone into water, ozone being given by an ozone generator.

From the above four versions, this paper refers to version III.

In version III, the oxygen required to increase the dissolved oxygen content in water is obtained by separating it from the air by adsorbing the N<sub>2</sub>, CO<sub>2</sub>, etc. with the help of absorbents called zeolites [2] [3].

## 2. Zeolites

The first natural zeolite called "stilbit" was discovered by V. Cronstedt in 1756 [2] [3].

Its property of losing constitution water by heating, with a boiling-like appearance, has led Cronstedt to adopt the name of zeolites (zoin = boil; lithos = stone) for this class of minerals.

For almost 100 years, the zeolites were considered mineral species whose interest was limited to mineralogical aspects only. During this time beside the stilbit, other natural zeolites were successively identified: natrolit, 1768; chabazit, 1772; harmoton, 1775; analcit, 1784, etc.

From a mineralogical point of view, today, under the name of zeolites, one of the most varied and extensive mineral families of the tectosilicate class consists of continuous three-dimensional networks of tetrahedral [SiO<sub>2</sub>] and [AlO<sub>4</sub>], which creates a rigid skeleton, opened, generally including cations that neutralize the excess negative charge of aluminium tetrahedral and water molecules.

Zeolites [3] are defined as "reticular aluminosilicates with ion-filled cavities and water molecules, which have considerable freedom of movement, allowing ionic exchange and gradual and reversible dehydration."

Natural zeolites are the result of endogenous or exogenous processes, which explains their spreading in volcanic and sedimentary rocks, in rocks of different types, ages and geological stages.

Our country has important zeolite deposits in the counties: Cluj, Sălaj, Bistrița-Năsăud, Bihor, Vrancea, Brașov and Prahova (Table 1.) [2].

Table 1. Natural zeolite deposits

No.	Name	Distribution
1.	Analcit	Tulgheşului Mountains, Moldova Nouă
2.	Canerinit	Ditrău, Ogradeva
3.	Chabazit	Muncelul Mic, Tebea, Moldova Nouă, Baia Mare, Bucharest
4.	Clinoptilolit	Mirşid-Sălaj, Pîglişa-Cluj
5.	Gmelinit	Techerău, Vălişoara, Balşa
6.	Epistilbit	Vaţa de Jos, Țihleş Mountains, Săcărâmb
7.	Heulandit	Poiana, Techerău, Căprioara
8.	Natrolit	Sviniţa, Techerău, Almaşul Mare, Plopiş
9.	Stilbit	Muncelul Mic, Moldova Nouă, Săcărâmb
10.	Stellerit	Poiana, Metalici Mountains

As far as the list of synthetic zeolites is concerned, it is much more difficult to establish, both because of the large number of new structures that are communicated annually and due to some misconceptions and misalignments. It can only be appreciated that their number is now over 100.

Synthetic zeolites are obtained by crystallizing hydrated aluminosilicates gels generally prepared from aluminate and silicate aqueous solutions or from reactive solid phases under various temperature and pressure conditions as well as artificial zeolitization of natural raw materials.

The researches on physicochemical properties of zeolites have found many uses as follows:

- Zeolite minerals have found a growing application in the field of environmental pollution reduction, based on their remarkable selectivity in adsorption and ion exchange.

Mordenite, clinoptilolite, chabazite is used for the enrichment of flowing and acoustic waters in oxygen, as well as for the generation of oxygen-enriched atmospheres used in the gasification of coal.

- Separation of gases

It is based on the molecular sieving effect and selective absorption depending on the shape, size and polarity of the molecules:

- Separation of aliphatic hydrocarbons (n-alkanes - iso-alkanes);
- Separation of lower alkanes from lower olefins with the same number of carbon atoms;
- Separation of aromatic hydrocarbons (especially xylene);
- Obtaining oxygen-enriched air or even component separation (N<sub>2</sub>, O<sub>2</sub>);
- Obtaining Ar of advanced purity;
- Removal of CO<sub>2</sub> and H<sub>2</sub>S from natural gas or synthesis gases;
- Chromatographic separation.

- In the cellulose and paper industry, clinoptilolite is added in a proportion of 28% to cellulose paste, resulting in increased whiteness and acid resistance of the paper. Clinoptilolite and mordenite are the basis of the paper used for electrostatic reproduction.

- The incorporation of natural zeolites in the composition of building materials, cement and low-density porous materials leads to the production of products with increased mechanical and chemical resistance.

- Clinoptilolite and phillipsite, as well as other natural zeolites, also find use in toothpastes, cosmetics, detergents, and many biochemical processes.

Since 1968, the natural gas purification method of compounds such as H<sub>2</sub>S, H<sub>2</sub>O, CO<sub>2</sub> using natural zeolites, competitive with the one based on monoethanolamine absorption but with large economic advantages, is used on an industrial scale. [3]

In agriculture and zoo technics, natural zeolites are used to obtain fertilizers capable of better nitrogen retention and a slow and controlled release of NH<sub>4</sub><sup>+</sup> ions.

### 3. Zeolites

By separating nitrogen from the air, a mixture of gases in volumetric ratio is obtained: O<sub>2</sub> =95%, N<sub>2</sub> =5%, at a pressure higher than atmospheric pressure by 5-7 m H<sub>2</sub>O; this separation takes place by passing a stream of air through a layer of zeolites; the device is called an oxygen concentrator.

Various types of oxygen concentrators have been made; A PLATINUM type oxygen concentrator (Figure 1) [4] will be used in the experimental installation.

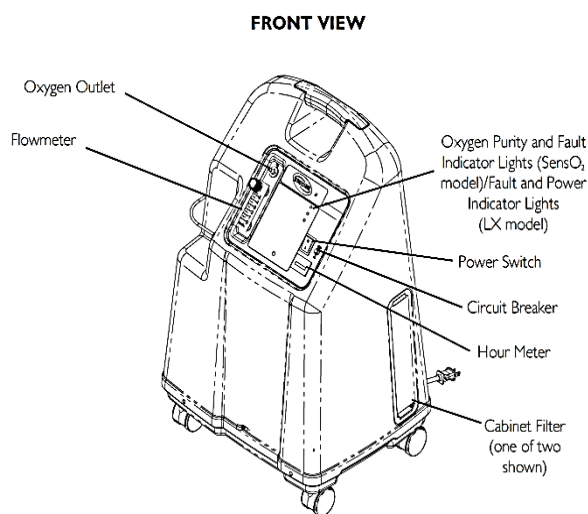


Figure 1: Oxygen concentrator type PLATINUM model IRC5LX02AWQ

Technical characteristics of the PLATINUM type oxygen concentrator model IRC5LX02AWQ:

a) Oxygen concentration level:

- Minimum 93% at 3 dm<sup>3</sup> / min;

- Minimum 91% at 4 dm<sup>3</sup> / min;

- Minimum 87% at 5 dm<sup>3</sup> / min.

b) Maximum oxygen pressure at the outlet of the device:

- 34.5 ± 3.45 kPa;

c) Volumetric flow rate: 0.5 ÷ 5 dm<sup>3</sup> / min;

d) Power consumption: 300W.

#### 4. Numerical Integration of the Equation of Oxygen Transfer Rate into Water

The oxygen transfer speed equation in water is [5]:

$$\frac{dC}{d\tau} = a \cdot k_L (C_s - C) \quad (1)$$

where:

C - The dissolved oxygen concentration at the time  $\tau$ ;

$a k_L$  -The volumetric mass transfer coefficient;

$C_s$  -The oxygen concentration in water at saturation.

The values of  $a k_L$  and  $C_s$  are constant with time. If the boundary conditions  $C = C_0$  for  $\tau = 0$  are imposed, the equation (1) can be integrated:

$$\frac{dC}{C_s - C} = a \cdot k_L d\tau \quad (2)$$

Assuming  $C < C_s$ , after integration, results:

$$-\ln(C_s - C) = a \cdot k_L \cdot \tau + ct \quad (3)$$

The  $ct$  term is obtained from the limit condition:

$$C = C_0 \quad \text{for } \tau = 0 \quad (4)$$

and has the value

$$ct = -\ln(C_s - C_0) \quad (5)$$

Inserting (5) into (3):

$$-\ln(C_s - C) = a \cdot k_L \cdot \tau - \ln(C_s - C_0) \quad (6)$$

$$\ln(C_s - C) = \ln(C_s - C_0) - a \cdot k_L \cdot \tau \quad (7)$$

$$\ln(C_s - C) = \ln(C_s - C_0) + \ln e^{-a \cdot k_L \cdot \tau} \quad (8)$$

$$\ln(C_s - C) = \ln((C_s - C_0) \cdot e^{-a \cdot k_L \cdot \tau})$$

$$C_s - C = (C_s - C_0) \cdot e^{-a \cdot k_L \cdot \tau}$$

$$C = C_s - (C_s - C_0) \cdot e^{-a \cdot k_L \cdot \tau} \quad (9)$$

initial:  $\tau = 0$ .

In the case of the study, gas is continuously introduced into the tank for 120 minutes, the regime is non-stationary,  $C_{O_2}$  increases in time.

In non-stationary regime, the measured amount is the concentration of oxygen in water in time. Measurements: water and air temperature, gas flow rate at the inlet of the tank and gas pressure in the body of the fine bubble generator.

Equation (9) has been numerically integrated by developing a computation program [6]. As initial data, the following are considered:

- The value of  $C_s$  is calculated from the relation [1]:

$$C_s = C \frac{k\%}{21\%} \quad (10)$$

where  $k$  represents the volumetric ratio of oxygen that diffuses in water ( $k = 95\%$ ).

For  $t = 29^\circ\text{C}$  and  $p = 760$  torr,  $C = 7.7$  mg / dm<sup>3</sup>, in the case of air with low nitrogen content:

$$C_s = 7.7 \frac{95\%}{21\%} = 34.8 \frac{\text{mg}}{\text{dm}^3} \quad (11)$$

- The initial concentration of dissolved oxygen in water at  $t_{H_2O} = 24^\circ\text{C}$  was  $C_0 = 5.84$  mg / dm<sup>3</sup>.

- The gas flow rate introduced into the fine bubble generator: 5 dm<sup>3</sup> / min = 300 dm<sup>3</sup> / h; two concentrators will deliver  $2 \times 300$  dm<sup>3</sup>/h = 600 dm<sup>3</sup>/h of which:

• 95% O<sub>2</sub> (i.e. 570 dm<sup>3</sup> / h);

• 5% N<sub>2</sub> (ie 30 dm<sup>3</sup> / h).

Total 600 dm<sup>3</sup> / h

After running the computation program, it was possible to draw the function  $C_{O_2} = f(\tau)$  in figure 2.

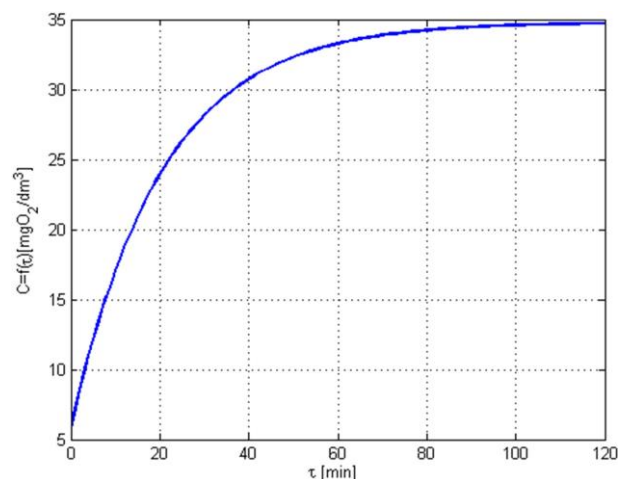


Figure 2: Graphical representation of variation in dissolved oxygen concentration in water in time

The curve  $C_{O_2} = f(\tau)$  and the obtained values satisfactorily coincide with other data in the literature [6] [7] [8].

The above obtained theoretical results will be experimentally verified in paragraph 6.

## 5. Description of the Experimental Installation

Figure 3 shows the scheme of the experimental installation.

Oxygen concentrators (1) deliver  $5 \text{ dm}^3 / \text{min}$  i.e.  $300 \text{ dm}^3 / \text{h}$  each, so the installation delivers a flow rate of  $600 \text{ dm}^3 / \text{h}$  at  $p > p_{\text{atm}}$ .

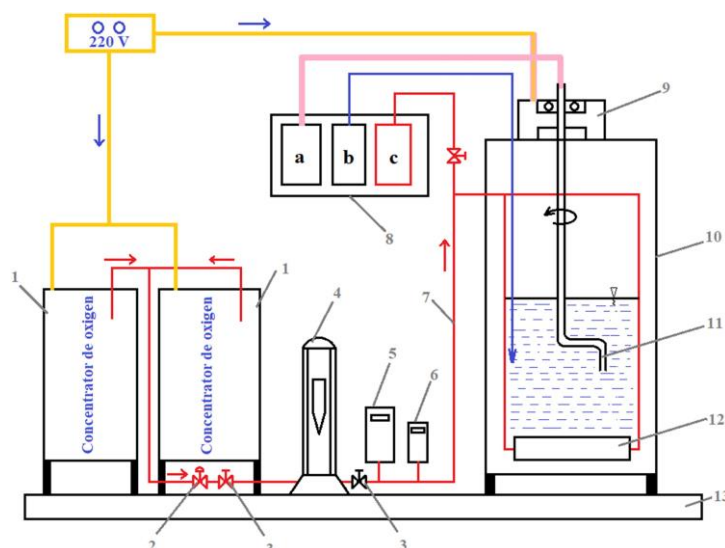


Figure 3: Scheme of the experimental installation for researches on water oxygenation  
 1 - oxygen concentrators; 2 - pressure regulator; 3 - valves; 4 - rotameter; 5- manometer with digital indication; 6 - digital thermometer; 7 - compressed air duct; 8 - panel with devices; a-oxygen meter; b - thermometer; c-manometer; 9 - electromechanical mechanism for probe oxygen sensor actuation; 10- water tank; 11 - oxygen probe; 12 - fine bubble generator; 13 - experimental installation support plate.

On the compressed air route to the fine bubble generator there are measuring devices for pressure (5), temperature (6) and compressed air flow rate (4); for measuring the air pressure in the fine bubble generator the device (8, c) was provided. The water temperature in the tank was measured with the device (8, b), and the dissolved oxygen concentration in water with the oxygenometer (8, a).

In the Oxygen Operating Manual, it is foreseen that during the measurements, the probe shall be displaced by  $0.3 \text{ m} / \text{s}$ ; it was necessary to construct an electromechanical mechanism for rotating the probe into the water tank by about  $2 \text{ rot} / \text{s}$  [9].

## 6. Purpose and Researches Methodology

### 6.1. Researches purpose

The researches aims to validate the theoretical results obtained in the previous calculations. The influence of the composition of the gas mixture (air + oxygen with reduced nitrogen content) on the variation in the dissolved oxygen concentration in water is studied.

This gas passes through the rotameter (4) and enters in the fine bubble generator on the position (12) located on the bottom of the water tank (10).

The air (5) (6) and water 8 (b + c) pressure and temperature are measured. For the operation of the air compressors within the oxygen generators 220V electric current is needed. Also for the movement of the oxygen probe in the water tank it is necessary to operate a mechanism [9].

### 6.2. Researches Methodology

For each measurement step the following phases are successively followed [10] [11] [12]:

1. Perform the bubble generator pressure test;
2. Fill the tank with water up to  $H = 0.5 \text{ m}$ ;
3. Measure the initial concentration of dissolved oxygen in water  $C_0 \text{ (mg / dm}^3\text{)}$ ;
4. Measure the water temperature in the tank and the air temperature;
5. Insert the fine bubble generator back and record the start time of the experiment;
6. The pressure and the compressed air flow rate are measured and maintained constants by means of control valves;
7. After 15 minutes, the oxygenation of the water is stopped and the oxygen probe is introduced into the water;
8. Start the electro-actuator of the probe that provides a speed of  $0.3 \text{ m} / \text{s}$ ; when the oxygen concentration value on the oxygen meter screen stabilizes, it means that the measurement has been completed;
9. Remove the oxygen probe from the tank;
10. Restart the oxygenation system and note the time.

From the experimental researches, it was found that by introduction an air flow  $V = 600 \text{ dm}^3/\text{h}$  into the water tank of  $H = 0.5 \text{ m}$  with a water volume  $0.5 \times 0.5 \times 0.5 = 0.125 \text{ m}^3$ , the dissolved oxygen concentration in the water approaches the saturation concentration after a time  $\tau = 2 \text{ h}$ .

The dissolved oxygen concentration in water was measured at equal time intervals:  $\tau = 0 \text{ min}$ ;  $\tau = 15 \text{ min}$ ;  $\tau = 30 \text{ min}$ ;  $\tau = 45 \text{ min}$ ;  $\tau = 60 \text{ min}$ ;  $\tau = 75 \text{ min}$ ;  $\tau = 90 \text{ min}$ ;  $\tau = 105 \text{ min}$ ;  $\tau = 120 \text{ min}$ .

The figure shows a picture of the experimental installation in which the two oxygen concentrators are operating and delivers  $2 \times 300 = 600 \text{ dm}^3 / \text{h}$  of gas (oxygen + nitrogen).



Figure 4: View of experimental installation

The results of the experimental measurements are shown in Table 1; it will be compared to the theoretical results obtained in paragraph 4.

Table 2. Title of the Table used for Exemplification

$\tau$ [min]	C [mg/dm <sup>3</sup> ]
0	5.84
15	20.1
30	27.2
45	31.0
60	32.5
75	33.1
90	33.6
105	33.8
120	34.1

Experimentally determined  $\text{CO}_2$  values are shown in Figure 9 through points.

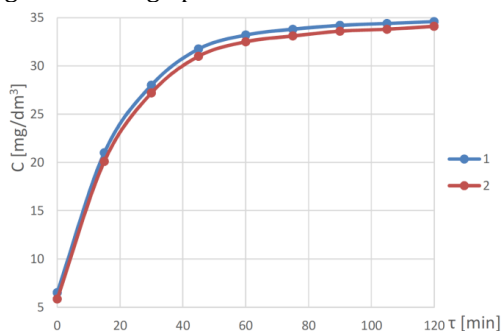


Figure 5: Graphical representation of variation in dissolved oxygen concentration in water in time  
1 - theoretical results; 2 - experimental results.

From Figure 5, one can observe a good coincidence between the theoretical and experimental results regarding the increase in dissolved  $\text{O}_2$  in water.

## 7. Conclusions

The most advanced method of water oxygenation is when pure oxygen is pumped into the water; the costs of using these methods are relatively high.

An efficient water oxygenation process is also achieved when air with low nitrogen content is introduced into the water.

Based on a technical-economic calculation, one can determine which solutions (1) or (2) are more advantageous, which will be solved in a future paper.

The graph  $C_{\text{O}_2} = f(\tau)$  is confirmed by many literature data [12] [13] [16].

Obviously, to reduce the oxygenation time, i.e. to reach the value of  $C_s$ , the percentage of 90%  $\text{O}_2$  must be increased to 100%.

The obtained experimental results are similar to those of other specialized papers [13] [14] [15].

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