

## APPLICATION OF A NEW TECHNOLOGY IN DRINKING WATER TREATMENT IN CITY TÂRGU CĂRBUNEȘTI

**Irina-Ramona Pecingină, University “Constantin Brâncuși”, Tg-Jiu, ROMANIA**  
**Roxana-Gabriela Popa, University “Constantin Brâncuși”, Tg-Jiu, ROMANIA**

**Abstract:** To assess the possibilities for the application of oxidation compounds to remove specific pollutants chloride ground source (in this case  $NH_4^+$  ions) from the Târgu Cărbunești were performed following experimental tests: THM formation potential establishment of individual sources with varying concentrations of natural organic compounds (dissolved organic carbon - DOC) and bromide ions in specific conditions and determine the evolution of the major pollutant, ammonium ions (concentrations of the order of mg/l) in the presence of agents chloride ( $Cl_2$ ,  $NaClO$ ) in different working conditions (dose, contact time, pH) outlining the steps the department for treatment.

**Key words:** pollutant, water treatment, drinking water

### 1. INTRODUCTION

Water is a fundamental and indispensable constituent of the human body. Small changes produce serious disturbances and insufficient water intake is much less tolerated than in other deficiency. Among toxins circulating through the water, some have natural origin, but most come from pollution of aquifers.

Water supply system in the city of Târgu-Cărbunești has three components:

- water catchment system;
- wastewater treatment and water pumping;
- transmission and distribution network of water to consumers.

#### **Water catchment system**

The collection is composed of eight deep boreholes, water collection network from wells and transport it to the treatment plant (fig.1.)



Figure 1. Abstraction of groundwater through wells in Targu-Cărbunești

#### **Water treatment plant and pumping**

Treatment plant and pumping is composed of:

- **raw water receiving device** - the snail-shaped metallic material

- **eration chamber** - having water dispensers mushroom made of metallic materials which have deteriorated requiring restoration
- **Slow settling chamber**
- **Fast filter room** where they are located three pools equipped with filtration filter (strainers) and degraded quartz sand to be replaced. In this room is a valve actuators filters (washing vats, tubs water inlet filters, water filters output valves, valve sewage). Quick filters Hall was refurbished in 2006 being in good condition (fig.3.)



Figure 3. Fast filter room

- **intermediary basin** (storage water treatment) with volume of 60 m<sup>3</sup> where water treatment is carried out with sodium hypochlorite an automatic injection (fig.4.)



Figure 4. Intermediary basin

- **pump room containing** (fig.5):
  - group treated basin water transfer intermediate in the central basin
  - washer pump group filters
  - city water distribution group (1) consists of Lowara pump (3 pieces) P = 4 kilowatt hours each
  - city water distribution group (2) consisting of pump Lowara P = 7.5 kW

- water analysis laboratory room, control room and control, electrical installation drive pump groups;
- central basin with a capacity of 750 m<sup>3</sup> (buried)



Figure 5. Room pumps

**Transport network and water distribution to consumers** it is made mostly of metal material pipe diameters from 219mm-50mm.

### 3. MATHERIALS AND METHODS

To assess the possibilities for the application of oxidation compounds to remove specific pollutants with chlorine ground source (in this case NH<sub>4</sub><sup>+</sup> ions) from the Târgu Cărbunești were performed following experimental tests:

- Establishment of THM formation potential of individual sources with varying concentrations of natural organic compounds (dissolved organic carbon - DOC) and bromide ions in specific conditions;
- Determining the evolution of pollutant majority ammonium ions (concentrations of the order mg/l) in chloride agents (Cl<sub>2</sub>, NaClO) in different working conditions (dose, contact time, pH) outlining steps treatment chain.

#### 3.1. ASSESSING THE POTENTIAL FOR FORMATION OF TRIHALOMETHANES (THM)

In the treatment with compounds chloride natural resources of drinking water (groundwater, surface) in one/two step generates organochlorine by-products

category, the most famous being the type derivatives trihalomethanes (THM MAC for total = 100 mg / l). Among the most important classes of organic THM precursors stated: humic acids (MON = natural organic matter), phenolic compounds, metabolites algae, aniline and derivatives etc. The reactivity of humic acids in the reaction is THM formation is given by the specific units of the type existing in the structure of polyhydroxy benzene (1 mg humic acids may typically 25 ± 4 g / l of chloroform). The main reactions of organic precursors with chlorine oxidation reactions are partial / total, substitution and addition. Assays THM formation potential in the treatment of chlorine (chlorine water) were made for the following sources:

- F3 (DOC = 1,55 mg C/l, Br<sup>-</sup> = 0,16 mg/l, N-NH<sub>4</sub><sup>+</sup> = 2,9 mg/l)

- F6 (DOC = 1,64 mg C/l, Br<sup>-</sup> = 1,17 mg/l, N-NH<sub>4</sub><sup>+</sup> = 10 mg/l)

- F7 (DOC = 4,49 mg C/l, Br<sup>-</sup> = 1,12 mg/l, N-NH<sub>4</sub><sup>+</sup> = 9,7 mg/l)

- F8 (DOC = 1,44 mg C/l, Br<sup>-</sup> = 0,11 mg/l, N-NH<sub>4</sub><sup>+</sup> = 3,3 mg/l)

Working conditions were:

- total mass - Cl<sub>2</sub>: DOC = 15: 1

- contact time 5 days

- ambient temperature (laboratory)

- pH 7 (buffer pH correction 7.2)

We worked with the water of chlorine (Cl<sub>2</sub> = 2.2 g/l) properly dosed organic carbon concentration water samples tested. After correction of the pH of the reaction vessels (glasses iodine) were kept in the dark, stirring occasionally. The parameters analyzed were:

- residual chlorine
- pH (after 3, 4 and 5 days)
- trihalomethanes
- ammonium hydroxide (after 4 or 5 days)

### 3.2. CHEMICAL OXIDATION METHOD CHLORIDE COMPOUNDS

➤ Oxidation of NH<sub>4</sub><sup>+</sup> to chlorine (chlorine water) Although the oxidation of NH<sub>4</sub><sup>+</sup> to chlorine break-point is not recommended in the literature to high concentrations of pollutant (NH<sub>4</sub><sup>+</sup> > 2 mg/l), and tests were performed for the evaluation of the experimental conditions for the treatment of underground sources at concentrations of about 6 mg NH<sub>4</sub><sup>+</sup>/l (chlorine doses, pH evolution, color changes, oxidation efficiency, byproducts, etc.). In this context, we used the water of chlorine (Cl<sub>2</sub> = 1.4 g/l, Cl<sup>-</sup> = 7.3 g/l). It is noted that prior to each test and analytical determinations were made of the concentration of the oxidant (Cl<sub>2</sub> in aqueous solution) and the pollutant (NH<sub>4</sub><sup>+</sup> in the raw water). Tests were aimed:

- evolution of the residual concentration of NH<sub>4</sub><sup>+</sup> ions at a dose corresponding to a Cl<sub>2</sub>:N-NH<sub>4</sub><sup>+</sup> = 8,2:1 (= 41 mg Cl<sub>2</sub>/l), while the determination of free residual chlorine, chloride and trihalomethanes;

- Setting parameters evolution pH, NH<sub>4</sub><sup>+</sup>, color depending on the dose of chlorine applied at constant contact time.

It is noted that the use of larger doses of 10 mg Cl<sub>2</sub> lead to displacement in the acid pH, being necessary in this case a correction of the pH level. Correction agents have been used 5% solution of NaOH or Na<sub>2</sub>CO<sub>3</sub> = 10 %.

### 3. RESULTS AND DISCUSSION

The results of analyzes performed to assess the *potential formation of trihalomethanes* (THM) are presented in tables 1 and 2 centralized

Table 1. Evolution THM concentration in Cl<sub>2</sub> report: DOC = 15: 1 after 4 days and 5 days of contact

Sample	CHCl <sub>3</sub>	CHCl <sub>2</sub> Br	CHClBr <sub>2</sub>	CHBr <sub>3</sub>	total THM	% majority species
F3/4	7,13	2,69	1,59	0,59	12,00	59 % CHCl <sub>3</sub>
F3/5	8,3	2,83	1,78	0,71	13,62	61 % CHCl <sub>3</sub>
F6/4	6,7	0,8	1,86	12,6	21,96	57 % CHCl <sub>3</sub>
F6/5	6,87	1,1	1,9	13,29	23,16	57 % CHCl <sub>3</sub>
F7/4	10,9	404	1,63	2,1	418,63	97 % CHCl <sub>2</sub> Br
F7/5	12	573	2,3	3,4	590,7	97 % CHCl <sub>2</sub> Br
F8/4	9,4	8	<0,1	<0,1	17,4	54 % CHCl <sub>3</sub> 46 % CHCl <sub>2</sub> Br
F8/5	11,3	9,3	<0,1	<0,1	20,6	55% CHCl <sub>3</sub> 45% CHCl <sub>2</sub> Br

Table 2. The evolution of indicators pH, free residual chlorine and  $\text{NH}_4^+$  in groundwater samples treated with chlorine

Sample	pH			$\text{Cl}_2$ free residual, mg/l			$\text{NH}_4^+$ , mg/l		
	3 days	4 days	5 days	3 days	4 days	5 days	3 days	4 days	5 days
F3	7,10	7,1	7,15	0,76	0,26	0,16	3,73	0,78	0,3
F6	7,18	7,2	7,29	0,52	0,5	0,44	13	7,49	6,67
F7	7,11	7,11	7,13	3,64	2,0	1,38	12,5	0,45	0,16
F8	7,90	7,95	8,04	0,8	0,3	0,18	4,28	0,89	0,5

The data presented in tables highlights the following:

- F7 source (DOC = 4.49 mg C/l,  $\text{Br}^-$  = 1.12 mg / l) has the highest concentration trihalomethanes, exceeding more than 5 times the CMA (THM = 100 mg/l);
- dissolved organic materials (DOC = 4.49 mg C / l) generates an appreciable amount of THM, the  $\text{CHCl}_2\text{Br}$  majority (97%).
- other sources (F3, F6, F8) and DOC values <2 mg/l, concentrations not greater than THM 30 mg / l, pointing out the differences in the speciation THM, depending on the initial concentration of ion- $\text{Br}^-$  nature organic loading and specific context:
  - Source F3 (DOC = 1,55 mg C/l,  $\text{Br}^-$  = 0,16 mg/l) – total THM (5 days) = 14  $\mu\text{g/l}$  (59 %  $\text{CHCl}_3$ );
  - Source F6 (DOC = 1,64 mg C/l,  $\text{Br}^-$  = 0,11 mg/l) – total THM (5 days) = 23  $\mu\text{g/l}$  (57 %  $\text{CHCl}_3$ );
  - Source F8 DOC = 1,44 mg C/l,  $\text{Br}^-$  = 0,11 mg/l) – total THM (5 days ) = 21  $\mu\text{g/l}$  (57 %  $\text{CHCl}_3$ , 45 %  $\text{CHCl}_2\text{Br}$ ).

- In the context of specific reactions and oxidation / chlorination organic load (ratio  $\text{Cl}_2$ : DOC),  $\text{NH}_4^+$  oxidation occurs and with variable returns:
  - F3, F8 ( $\text{NH}_4^+_{i} \leq 4,3$  mg/l)  $\eta\text{NH}_4^+ = 88 - 92$  %
  - F7 ( $\text{NH}_4^+_{i} = 12,5$  mg/l)  $\eta\text{NH}_4^+ = 99$  %
  - F6 ( $\text{NH}_4^+_{i} = 13$  mg/l)  $\eta\text{NH}_4^+ = 49$  %
- Residual concentration of  $\text{Br}^-$  ions are below the limit of the method ( $\text{Br}^- < 0.1$  mg/l) sources of F3, F6 F7 and F8, and the source has a non-volatile concentration of  $\text{Br}^- = 0.59$  mg/l ( $\eta$  oxidation=50%).

Preliminary data indicates high potential for groundwater trihalomethanes formation in drilling F7, which is composed of natural organic substances organoclorurați generating by-products in the context of the presence of bromide ion.

As regards the second method, *oxidation of  $\text{NH}_4^+$  + to chlorine (chlorine water)*, the results of a constant dose of chlorine (41 mg  $\text{Cl}_2$ /l) at contact times of 30-50 minutes and after 19 hours are shown in table 3 and figure 6.

Table 3. Experiments  $\text{NH}_4^+$  oxidation with chlorine. Influence of contact time ( $\tau = 30$  min, 40 min, 50 min 19 hours) - dose = 41  $\text{MgCl}_2$  / l

Parameter	Values determined					Observations
	$A_{p/0}$	$A_{p/30}$	$A_{p/40}$	$A_{p/50}$	$A_{p/1140}$	
pH	7,53	7,68	7,63	7,63	7,6	pH correction agent NaOH5% ( $\rho = 1.08$ g / $\text{cm}^3$ ) Consumer NaOH5% - 1.6 ml / l (pHi = 5.9 - after the dosage of chlorine water) Chlorine water - 1,4 g $\text{Cl}_2$ /l - 7,3 g $\text{Cl}^-$ /l
Turbidity, UNT	11,4	9,9	9,2	9,1	8,1	
$\text{NH}_4^+/\text{N}-\text{NH}_4^+$ ,mg/l	6,45/5	4,1/3,2	2,56/2	0,1/0,07	0,05/ -	
$\text{Cl}_2$ free residual (mg/l)	-	10	8	6,5	1	
$\text{Cl}^-$ ,mg/l	40,5	285	289	292	360	
THM	-	7,4	8	9,37	16,75	

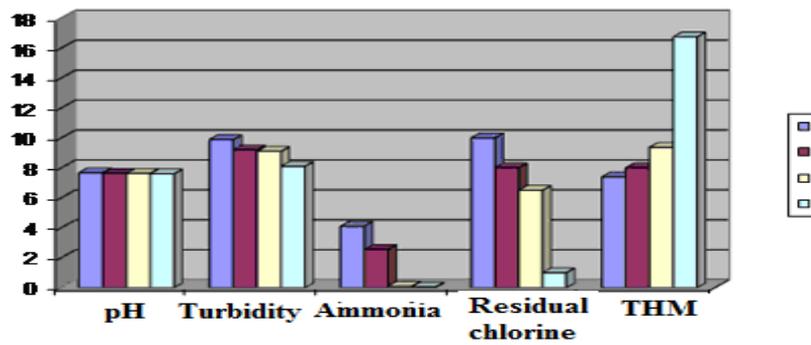


Figure 6. Graphical representation of  $\text{NH}_4^+$  + oxidation experiments with chlorine

From the data presented, the following issues were highlighted:

- Addition of the solution of the oxidant (chlorine water) cause a decrease in pH from pH 7.5 to pH 5.9 and pH correction was made with 5% NaOH solution (1.6 ml / l) at a value close to the initial pH ( $\text{pH}_i = 7.68$ );
- residual concentration of  $\text{NH}_4^+$  + decreases progressively with increasing contact time ( $\tau = 30$  min,  $\eta_{\text{NH}_4^+} = 36\%$ ,  $\tau = 40$  min,  $\eta_{\text{NH}_4^+} = 60\%$ ,  $\tau = 50$  min,  $\eta_{\text{NH}_4^+} = 98\%$ );
- Free residual chlorine is maintained at high values of the order of mg / l, with decreasing trend ( $\tau = 50$  min,  $\text{Cl}_2 = 6.5$  mg / l), reaching after 19 hours of contact at 1 mg / l;
- The concentration of chlorine in treated water increases significantly, exceeding the maximum permissible limit (CMA  $\text{Cl}^- = 250$  mg / l);
- Trihalomethanes (THM total) dial is at the level of mg / l - tens mg / l, showing an increasing trend, below normal (CMA  $\text{THM}_t = 100$  mg / l)

Also, tests were conducted to check the influence of the dosage of oxidant ( $\text{Cl}_2 = 5$  to 30 mg/l) of pH indicator, color,  $\text{NH}_4^+$   $\tau$  residual contact time = 30 min, to follow the development of color over time.

Physico-chemical analyzes are shown in tables 4 and 5.

Table 4. Experiments NH<sub>4</sub><sup>+</sup> + oxidation with chlorine. Influence of oxidant dose on pH indicators, color, NH<sub>4</sub><sup>+</sup> yield  $\tau = 30$  min

Parameter	Values determined at various doses of Cl <sub>2</sub>						Observations	
	0 mg Cl <sub>2</sub> /l	5 mg Cl <sub>2</sub> /l	10 mgCl <sub>2</sub> /l	15 mg Cl <sub>2</sub> /l	20 mg Cl <sub>2</sub> /l	30 mgCl <sub>2</sub> /l		
pH	7,51	7,16	6,85- correction 7,42	6,65- correction 7,31	6,45- correction 7,42	6,14- correction 7,43	Agent correction pH Na <sub>2</sub> CO <sub>3</sub> 10 %  ( $\rho = 1,11$ g/cm <sup>3</sup> )	
Cl <sub>2</sub> , free residual (mg/l)	-	0,6	0,7	0,9	1,2	4,6		
NH <sub>4</sub> <sup>+</sup> (mg/l)	5,75	4,82	2,83	1,3	0,7	<0,05		
Color, m <sup>-1</sup>	$\lambda = 436$ nm	0,7	4,9	6,5	7,2	8,3		8,9
	$\lambda = 525$ nm	0,2	2,7	2,7	2,8	3		3,3
	$\lambda = 620$ nm	0	2,4	2,7	2,9	3,2		3,2
Na <sub>2</sub> CO <sub>3</sub> 10 %, ml/l	-	-	0,25	1,5	2	3		

Table 5 Experiments NH<sub>4</sub><sup>+</sup> oxidation with chlorine (dose: 5 MgCl<sub>2</sub> /l to 30 mgCl<sub>2</sub> / l), Color development time ( $\tau_1 = 30$  min,  $\tau_2 = 60$  min,  $\tau_3 = 19$  hours)

Doze Cl <sub>2</sub> ,mg/l	Color evolution (m <sup>-1</sup> )									Observations
	$\tau = 30$ min			$\tau = 60$ min			$\tau = 19$ hours			
	436 nm	525 nm	620 nm	436 nm	525 nm	620 nm	436 nm	525 nm	620 nm	
5	4,9	2,7	2,4	0,8	0,5	0,4	0,7	0,2	0,2	Color raw water (A <sub>p</sub> ) $\lambda = 436\text{nm}-0,7$ m <sup>-1</sup> $\lambda = 525\text{ nm}-$ 0,2m <sub>1</sub> $\lambda = 620\text{ nm}-0,0$ m <sup>-1</sup>
10	6,5	2,7	2,7	0,7	0,5	0,3	0,7	0,4	0,4	
15	7,2	2,8	2,9	0,8	0,5	0,4	0,7	0,4	0,4	
20	8,3	3	3,2	0,8	0,5	0,4	0,7	0,5	0,5	
30	8,9	3,3	3,2	2,7	0,6	0,4	0,8	0,5	0,5	

The data presented show the following aspects:

- application of chlorine doses > 10 mg Cl<sub>2</sub>/l leads to lower pH, implying its correction;
- pH correction to values similar to raw water pH was done with Na<sub>2</sub>CO<sub>3</sub>, 10% (from 0.25 to 3 ml / l);
- concentration of ammonium (NH<sub>4</sub><sup>+</sup> and 5.75 mg/l) decreases gradually with increasing dose of chlorine used and efficiencies increased from 16% (Cl<sub>2</sub> dose = 5 mg/l) than 99% (the dose Cl<sub>2</sub>=30 mg/l);
- free residual chlorine increases with increasing chlorine dose of 0.6 mg / l to 4.6 mg / l;
- increasing the dose of chlorine leads to the development of yellow color in particular,  $\lambda = 436$  nm determined that after 60 minutes of contact, as it consumes chlorine disappears (almost identical raw water) except the sample with the highest dose of chlorine (30 mg Cl<sub>2</sub> / l), the discoloration occurs after 19 hours of contact (table 5).

## 4. CONCLUSIONS

To assess the possibilities for the application of oxidation compounds to remove specific pollutants chloride ground source (in this case  $\text{NH}_4^+$  ions) from the Târgu Cărbunești were performed following experimental tests:

- THM formation potential establishment of individual sources with varying concentrations of natural organic compounds (dissolved organic carbon - DOC) and bromide ions in specific conditions
- determine the evolution of the major pollutant, ammonium ions (concentrations of the order of mg/l) in the presence of agents chloride ( $\text{Cl}_2$ ,  $\text{NaClO}$ ) in different working conditions (dose, contact time, pH) outlining the steps the department for treatment.

In the treatment with compounds chloride natural resources of drinking water (groundwater, surface) in one/two step generates organochlorine by-products category, the most famous being the type derivatives trihalomethanes (THM MAC for total = 100 mg / l).

Although the oxidation of  $\text{NH}_4^+$  to chlorine break-point is not recommended in the literature to high concentrations of pollutant ( $\text{NH}_4^+ > 2$  mg/l), and tests were performed for the evaluation of the experimental conditions for the treatment of underground sources at concentrations of about 6 mg  $\text{NH}_4^+$ /l (chlorine doses, pH evolution, color changes, oxidation efficiency, byproducts, etc.). In this context, we used the water of chlorine ( $\text{Cl}_2 = 1.4$  g / l,  $\text{Cl}^- = 7.3$  g/l).

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