DRINKING WATER TREATMENT BY BULGARIAN PRODUCTS IN BULGARIA AND TURKEY

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ABSTRACT

Drinking water treatment by aluminum sulphate has not only technical disadvantages but also health risks. The recently postulated apparent association between aluminium levels in the brain with Alzheimer's disease and the distressing aftermath of the Camelford incident, has thrown open the question of the magnitude of any risk from aluminium exposure in drinking water. Doubts have also arisen about the safety, using the flocculents based on polyacrylamide. The reason is its acrylamide monomer content. For these valid reasons the new Bulgarian coagulant OAX-15 has been created in the 1976 (Kungl Patent 77 12594-6-OCH, 1982 and Patent 61018-OCH, 1987). The drinking water station " Kamchia", supplied the Black Sea cities Varna and Burgas, first changed the aluminium sulphate by OAX-15.

The author of this paper, rendering an account the additional necessity of flocculents or sorbents for some heavy polluted waters, made one new revised Bulgarian product CFS-Solvo (Sanitary certificate, 1995).

Jar-tests and physic-chemical treatment in the Bulgarian and Turkey drinking water stations showed the effectiveness of the CFS-Solvo for elimination of turbidity, colour, oxydizability, arsenium, manganese, heavy metals, plankton etc. for water temperature from 1^0C to 30 ^{0}C. The measured value of residual aluminium was from 0,0 to 0,1 mg/l.

In the paper are discussed the technological and sanitary priorities of CFS drinking water treatment over the aluminium sulphate treatment. The results are very perspective for quality amelioration of drinking waters on the Black Sea coast.

KEYWORDS

Drinking water treatment, coagulation, aluminum sulfate, polyaluminum chloride,
Coagulant-flocculent-sorbent CFS,

INTRODUCTION

The coagulation is the basic stage of drinking water treatment. Last century different types of coagulants and flocculents has been used but the most common coagulants are based on inorganic hydrolization salts. Aluminum sulfate is more frequently applicated coagulant of this class. Its drinking water usage is related with very big exploitation disadvantages and higher health risk. The limited working scopes of pH and temperature hamper the creation of stable flocculation particles with necessary dimensions. Very often at the temperature below 10 ^{o}C and pH outside of 7 – 8 the bad flocculation process costs a second coagulation into the filters and pipes after the stations. This effect makes drinking water worse and blocks very fast the filter layers. At the drinking water stations with stabilization stage the aluminum sulfate's coagulation is embarrassed. Health risk – the content of aluminum higher than 0.2 mg/l in the treated water is observed when the optimum conditions are drawed away (Association General des Hygienists et Technicians Municipals, 1987). The recently postulated apparent association between aluminum levels in the brain with Alzheimer's disease and the distressing aftermath of the Camelford incident, has thrown open the question of the magnitude of any risk from aluminum exposure in drinking water (Holdsworth, 1991). These shortcomings impose the looking for and finding out the polyaluminum chloride as one of the alternative coagulant (Kogyo Yosui,1974).

PRODUCTION OF CFS-SOLVO®

At the second part of seventeen the production of Bulgarian polyaluminum chloride OAX-15 was done (Patent 77 12594-6-OCH, 1982 and Patent 61018-OCH,1987). Former capacity productions were as follows: factory "Sviloza", town Svichtov – 5000 t/y and Ecological Technique Center, town Burgas- 2500 t/y.

The technology of AOCl-15 production is as follows: in the intern electrolyse conditions a metallic aluminium is dissolved by HCl.

The metallic aluminum is nonstable thermodynamically - transformation into water solution as $Al(H_2O)_6^{3+}$ at salinity acid circle. Different polynuclears aquahydroxoaluminum complex ions are formed as a result of polycodensation processes. The reaction between aluminum and HCl in water circle is very complicated and debatabled. In this paper the reaction is described provisionally as follows:

$$2Al + 6HCl = 2AlCl_3 + 3H_2 \qquad (1)$$

$$x[Al(H_2O)_6]^{3+} = Al_x(OH)_y(H_2O)_{2(3x-y)}]^{(3x-y)+} + yH_3O^+ \qquad (2)$$

At 1994 on the base of preliminary experience of polyaluminum chloride synthesis the Solvo-Ltd, town Sofia, was beginning the production of very effective coagulant-flocculent-sorbent CFS-Solvo.
CFS is done on the base of polyaluminum chloride and its description very generally is :

$$xAl_2O_3.yHCl.zH_2O \quad (x=1,\ y=0.9\text{-}2,\ z=4\text{-}85);\ M=y/x \qquad (3)$$

CFS solution is stable at middle and high concentrations including also the glassy state. After alkalisation or dilution the hydrolic processes begin to leak. As a result are obtained decantabled very small soluble hydroxosalts and aluminum hydroxide. Received hydrolysed products have not only sorbtion ability but also an ability of codecantation of different particles by type and dimension.

At 1994 Solvo Ltd, town Sofia, designed and investigated a new apparatus for CFS's electrochemical synthesis at very high level of process regulation and energy utilisation (Fig. 1). On the base of the first constructed apparatus Solvo Ltd created the module industrial installation for CFS production. Each installed module at open air condition produces 2 t/d CFS.

CFS has sanitary permition for treatment of drinking and waste waters (Sanitary certificate,1995).

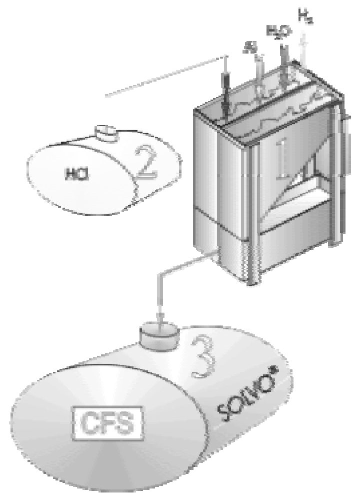

FIG. 1. SCHEME OF TECHNOLOGY FOR CFS'S PRODUCTION:
1- REACTION CHAMBER, 2- HCL TANK AND 3 – CFS TANK

DETERMINATION OF CFS DOSES

Determination of CFS's dose is made by the quantity of active product as Al_2O_3. This method of calculation is obligatory because CFS is nonstechiometric product – without any exact molecule weight. Also, the comparison with aluminum sulfate's doses have to be done by Al_2O_3 content.
The procedure of CFS Jar-test is as follows:
To one liter of simple waters it has to be added different doses of trade product CFS. It's not preferable a preliminary dilution of CFS by water. The reason is a big damage of CFS's hydrolization before entering into treated water.
Two stages of CFS Jar-test is necessary:

- 30 min. slow mixture (about 20 tours/min);
- 30 min decantation.

Very good decantated water has to be taken for water analysis.
Calculation of CFS's dose is made on the base of the relation between density, acidity M (M=mol HCl/mol Al_2O_3) and percentage content of Al_2O_3 (Fig.2).

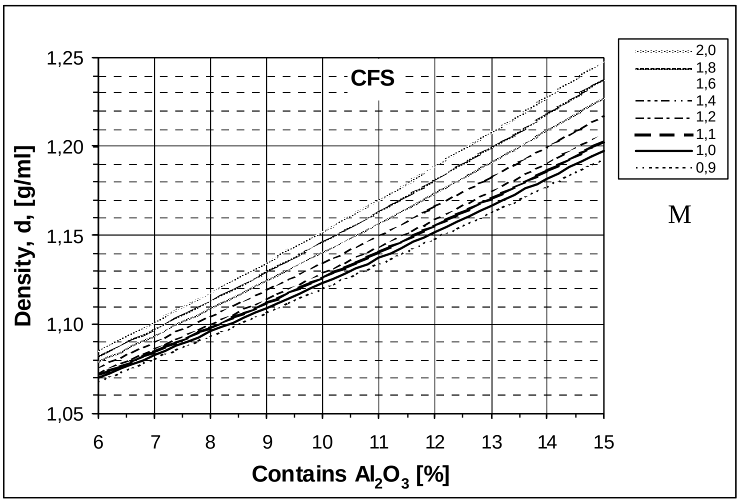

FIG. 2. RELATION BETWEEN DENSITY, ACIDITY AND AL_2O_3 OF CFS SOLUTION

CFS's application at drinking water stations doesn't need a preliminary dilution or an intensive mixture. CFS can be used not only alone. It's possible to combine the CFS with other chemical products.

For example, we describe the Jar-test of dam Iskar's waters by CFS and $Al_2(SO_4)_3.18H_2O$, made at 03.01.1995 to the Laboratory of drinking water station "Pancharevo", town Sofia. The concentrations and the relatively weights of two products are shown in the Table 1.

TABLE 1 CONCENTRATION AND DENSITY
OF CFS AND ALUMINUM SULFATE – TRADE PRODUCTS

Type of product	Concentration [%]		Density $[g/cm^3]$
	Al_2O_3	$Al_2(SO_4)_3$	
CFS13	13		1.18
CFS10	10		1.14
AS = $Al_2(SO_4)_3$	6.3	21.1	1.17

Data for applicable doses and purification effects of dam "Iskar" water (pH 7.0, turbidity 3.9 mg/l, color 22^o, oxydability 1.8 mg O_2/l and manganese 0.37 mg/l) by Aluminum sulfate and CFS are done in Tables 2,3..

TABLE 2 CALCULATION OF DOSES, CORRESPONDING TO 2.3 mg Al_2O_3/l

No	Water test by	DOSES							Total
		CFS			$Al_2(SO_4)_3$				
		ml/l (dm/m^3)	mg/l (g/m^3)	Al_2O_3 mg/l	ml/l (dm/m^3)	mg/l (g/m^3)	AS mg/l	Al_2O_3 mg/l	Al_2O_3 mg/l
1	CFS13	0.015	17.7	2.30	-	-	-	-	2.30
2	CFS10	0.020	22.8	2.28	-	-	-	-	2.28
3	AS	-	-	-	0.031	36.3	7.67	2.29	2.29
4	CFS10+AS	0.006	6.84	0.68	0.022	25.7	5.42	1.62	2.30
5	AS+ CFS10	0.006	6.84	0.68	0.022	25.7	5.42	1.62	2.30

TABLE 3 JAR-TESTS OF DAM "ISKAR" WATER BY ALUMINUM SULFATE
AND CFS AT DRINKING WATER STATION "PANCHAREVO", TOWN SOFIA

	Water test by	Quality of treated water								
		pH	Turbidity		Color		Oxydability		Manganese	
			Value	Effect	Value	Effect	Value	Effect	Value	Effect
			mg/l	%	^{o}Rubyov	%	mgO_2/l	%	mg/l	%
0	Dam water	7.0	3.9	-	22	-	1.80	-	0.37	-
1	CFS13	7.0	1.1	72	3	86	1.22	32	0.19	49
2	CFS10	7.0	1.4	64	3	86	1.22	32	0.22	40
3	AS	6.9	1.7	56	6	73	1.36	24	0.22	40
4	CFS10+AS	7.0	1.2	69	4	82	1.30	28	0.20	46
5	AS+ CFS10	7.0	1.1	72	3	86	1.22	32	0.22	40

49% elimination effect of manganese is explained by low water turbidity (3.9 mg/l).
Former investigations at drinking water station "Pancharevo" created the exact diagram between dam water turbidity and manganese elimination effect (Fig. 3).

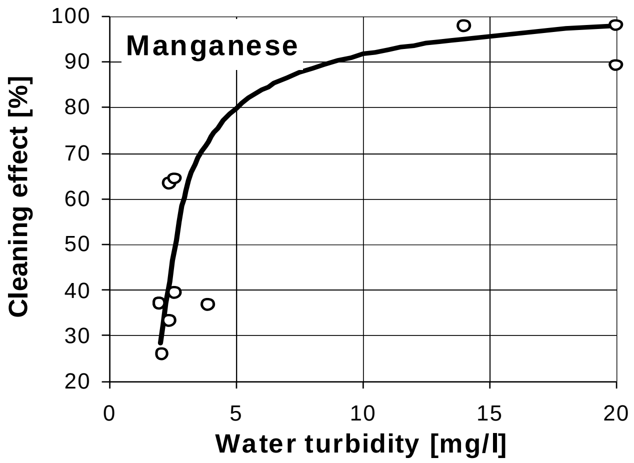

FIG.3. DIAGRAM FOR MANGANESE CLEANING EFFECT AND TURBIDITY OF DAM "ISKAR" WATER

It's obviously that 80% elimination of manganese is achieved at water turbidity higher than 5 mg/l.

CFS DRINKING WATER TREATMENT DATA

Laboratory and industrial investigations with Bulgarian and Turkey waters at the period from 1994 to now show very high elimination effectiveness of color, turbidity, oxydability, plankton, Fe, Mn, As, Cu, Cd, Hg, Pb, Ni, SO_4^{2-}, PO_4^{3-} etc. (Dobrev, 1994 and Dobrev, 1996).
The influence of water temperature on coagulation effect is demonstrated at low values in Bulgaria, town Sofia (1 ^oC , November/ December 1994 at Drinking water station "Pancharevo") and at high values in Turkey, town Istanbul (24 ^oC, June 1995 with dam "Alibay" waters and 15.2 ^oC, November 1997 with dam "Iski Kagithane" waters).
The results of Turkey's investigations by $Al_2(SO_4)_3.18H_2O$ and CFS are given in Tables 4,5.

TABLE 4 COMPARATIVE COAGULANT'S INVESTIGATIONS OF DAM "ALIBAY" WATERS AT TEMPERATURE 24 ^OC

Indices and coagulant's dose	Dam water	Type of used coagulant					
		$Al_2(SO_4)_3$	CFS- SOLVO®				
05.06.1995							
Dose, mg Al_2O_3/l	0	*4.8*	1.0	3.0	6.0	12	
pH	7.60	*7.40*	7.62	7.61	7.59	7.58	
Turbidity, NTU	3.80	*4.10*	3.40	1.80	0.75	0.70	
Oxydability,mgO_2/l	4.50	*4.15*	4.20	3.26	2.47	2.07	
Residual Al, mg/l	-	***1.20***	0.13	0.125	0.12	0.11	
06.06.1995							
Dose, mg Al_2O_3/l	0	*7.5*	1.0	2.0	5.0	10	20
pH	7.65	*7.31*	7.62	7.61	7.61	7.58	7.55
Turbidity, NTU	29.0	*2.7*	13.5	3.0	2.3	2.2	2.2
Oxydability,mgO_2/l	5.64	*3.96*	4.65	3.56	3.26	2.57	2.27
Residual Al, mg/l	-	***1.30***	0.11	0.10	0.095	0.080	0.075
08.06.1995							
Dose, mg Al_2O_3/l	0	*4.8*	2.0	4.0	6.0	8.0	10
pH	7.60	*7.41*	7.63	7.62	7.61	7.58	7.56
Turbidity, NTU	5.10	*2.60*	1.60	0.90	0.80	0.80	0.50
Oxydability,mgO_2/l	4.85	*4.36*	4.06	3.23	2.79	2.69	2.40
Residual Al, mg/l	-	***0.840***	0.070	0.062	0.060	0.055	0.045

TABLE 5 COMPARATIVE COAGULANT'S INVESTIGATIONS OF DAM "ISKI KAGITHANE" WATERS AT TEMPERATURE 15.2 ^{O}C

Indices and coagulant's dose	Dam water	Type of used coagulant			
		$Al_2(SO_4)_3$	CFS- SOLVO®		
11.11.1997					
Dose, mg Al_2O_3/l	0	*7.5*	1.0	2.0	5.0
pH	7.48	*7.07*	7.22	7.08	6.54
Turbidity, NTU	19	*4.30*	0.33	0.50	0.40
Oxydability,mgO_2/l	4.50	*3.52*	2.25	2.00	1.71
Residual Al, mg/l	0.042	***0.600***	0.100	0.097	0.130

The Sofia's drinking water experimentation by CFS was made at low temperature (1-2 ^{o}C) and low turbidity (2.5 mg/l) when Aluminum sulfate coagulation isn't possible (Dobrev, 1996). After dam water passing by station "Pancharevo" the quality of treated water didn't reply to BDS 2823-83 "Potable water" by the next parameters: oxydability, turbidity, color, iron, manganese and plankton. In Figure 4 as normal regime are shown the values of different pollutants at the beginning of station (dam water), after sedimentation tanks (pulsators) and after filters before chlorinating (treated water). By Solvo regime (coagulation by 10-20 ml CFS solution per one cubic meter water - 0.3 – 0.5 cents/m3) was obtained good water quality after Bulgarian potable water standard 2823 – 83 (Fig.4). Measured values of residual aluminum in treated water were between 0.0 – 0.04 mg/l.

From 1994 the technical and economical effectivenesses of CFS industrial usage has being proved at Drinking water station, town Kustendil.

DISCUSSION

The comparative investigations of coagulation of Turkey surface water (Alibay and Iski Kagithane dams waters) by Aluminum Sulfate and CFS showed the best results of treatment at higher temperature (24 ^{o} C), turbidity and oxydability. The pH drop is lower by CFS treatment. The value of residual aluminum is always lower than health norm. Big problem of aluminum sulfate treatment as seen in Tables 4,5 is the high value of residual Aluminum Sulfate in treated waters (to 1.3 mg/l).
Also, good results were obtained by CFS treatment of Bulgarian surface water (dam 'Iskar", town Sofia) at low temperature (1 ^{0}C) and turbidity and high content of plankton when Aluminum Sulfate is not applicable. Total elimination of manganese can be achieved at turbidity higher than 5 mg/l (Fig.3).
CFS can be used as a flocculent at Aluminum Sulfate treatment. Better results are obtained when CFS is added after Aluminum Sulfate (Table 3 – water sample 5).

CONCLUSIONS

The priorities of CFS's coagulation of Bulgarian and Turkey surface waters are as follows:
- without of any essential pH water changement;
- large optimum areas of pH, applicable doses and temperature;
- coagulation process is possible at low temperature (0.1 – 1.0 ^{0} C) and turbidity;
- easy and total elimination of iron and plankton at any cases;
- total manganese elimination is obtained at water turbidity higher than 5 mg/l and pH higher than 7;
- in the treated water there isn't any residual aluminum with health risk concentration;
- can be used as flocculent to Aluminum Sulfate treatment;
- technical and economical effectiveness.

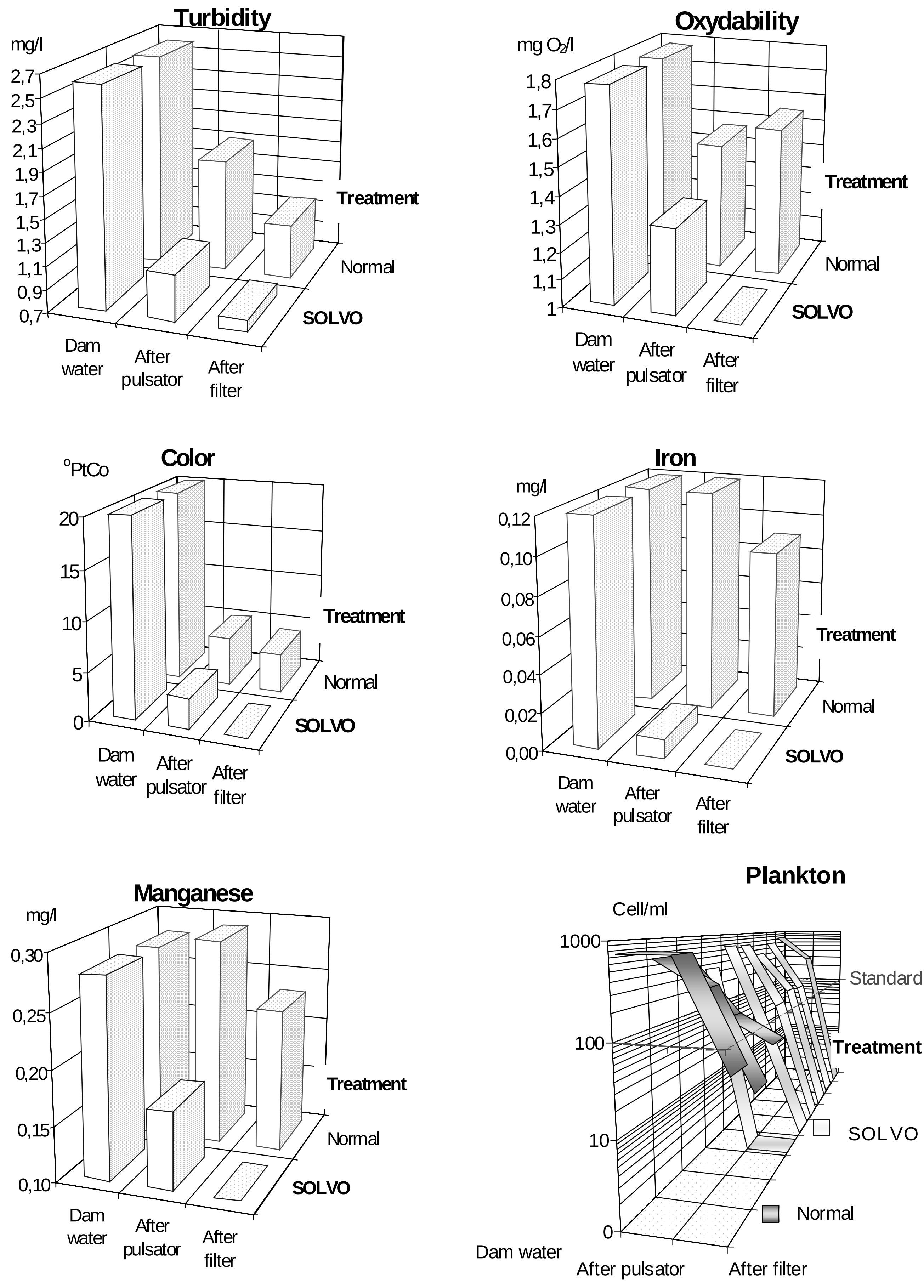

FIG. 4. DRINKING WATER TREATMENT AT PANCHAREVO STATION, TOWN SOFIA, BY CFS (NOVEMBER/DECEMBER 1994)

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