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CHANGES OF SOME SULPHURIC THERMAL WATER CHARACTERISTICS DUE TO CHLORINATION

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Positive and negative effects of water chlorination and aeration were examined in samples of sulphuric thermal water from rehabilitation pools. Although chlorination considerably improved the microbiological quality of the water, it caused various negative physical and chemical changes. Aeration caused loss of hydrogen sulphide and production of colloidal sulphur (milky turbidity), whereas chlorination developed a yellowish-reddish-brown colouring depending on chlorine dosage, and also provoked the disappearance of sulphides. It is concluded that sulphuric thermal water should not be chlorinated because of elimination, through chlorination, of therapeutically active compounds causing organoleptic changes that are subject to complaints from patients.

Key terms:
change of colour, chlorine dosage, free available chlorine, pool water, rehabilitation, sulphuric compounds, turbidity, water aeration

Since ancient times natural thermal mineral waters have been used for healing purposes, although how they affect the human organism is not entirely understood (1, 2). If such waters also contained components, like iodine, fluorine, sulphur, radon, radium etc, their healing properties were even greater. Such waters are used in different ways, most often at their very source as recreation or rehabilitation pools.

The quality of the water in recreation and rehabilitation pools in Croatia is subject to regulations that also hold for drinking water (3). It should be clear, free of turbidity, colour, deposits and of film at the surface (4).

Water disinfection is performed by means of oxidizing disinfectants. Those destroy microorganisms but also prevent the growth of algae and remove oxidizing

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substances that are brought in by bathers (5–7). The water hygiene is maintained by disinfection as well as by a daily addition of 5 per cent of fresh water out of the total pool water quantity. In the pools using recirculating water the water should be filtered and its entire quantity replaced in 6–8 hours' time (5).

In rehabilitation pools the water temperature is usually above 30 °C causing a fast decomposition of disinfectants. In addition to want of legal regulations, the pools used for medical rehabilitation have been reported to be poorly equipped (they often lack filtration, recirculation and chlorination systems), education of personnel and bathers has been found insufficient, disinfection measures inadequate, bathers' personal hygiene poor, bathing load heavy and sanitary control inefficient and irregular; the pools have been considered as places of risk to patients' health (8).

The permissible concentration of free available chlorine (FAC) in pool water depends on sanitary regulations, the epidemiological situation and other circumstances. Under Croatian legislation, chlorine should be maintained at 0.3–0.4 mg/L while in some other countries, like Sweden, the concentration is pH-dependent and may reach 0.4 mg/L or as much as 1.5 mg/L if the pH is over 8.5 (4, 9).

Pool water chlorination is not easy to carry out because it is a dynamic process, starting with a constant inflow of new bathers as well as of different biological and chemical pollutants, and undergoing changes in temperature, pH, alkalinity, chloride content, etc. The biological causative agents, which can be isolated from water, are different bacteria, viruses, fungi, protozoa, etc., and the most frequent chemical substances are nitrogenous compounds (ammonia, nitrites, urea, uric acid, chloramines) and chlorides.

In Croatian thermal rehabilitation pools, most of which have obsolete equipment and a small amount of thermal water, the fill-and-draw system on a daily basis is usually applied.

In addition, organoleptic problems arising in connection with sulphuric thermal waters, like change in colour and turbidity, are intensified by water chlorination and cause discomfort to bathers (personal communication).

Changes in sulphuric compounds due to water aeration

Sulphuric compounds in thermal waters undergo greatest changes as a consequence of physical-chemical reactions during water aeration (10–12). Sulphides can be present in water as H_2S and as HS^- and S^{2-} ions (10):

$$\text{Sulphides} = (H_2S + HS^- + S^{2-})$$

The hydrolysis of hydrogen sulphide in water depends on pH:

$$H_2S \leftrightarrow HS^- + H^+$$
$$HS^- \leftrightarrow S^{2-} + H^+$$

The higher the pH, the more dissolved the HS^- and S^{2-} in the water; the lower the pH, the more undissolved (i.e. released from water) the H_2S. Thus, at a pH

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below 5 practically all sulphide is present in the form of hydrogen sulphide, whereas at a pH above 9 it is present as dissolved sulphide. At pH 6.6, hydrogen sulphide accounts for 56 per cent of total sulphides (13). The water loses hydrogen sulphide during aeration (14).

With the loss of hydrogen sulphide from the water the disturbed balance of

$$H_2S \rightleftarrows HS^- \rightleftarrows S^{2-}$$

is reestablished by recombination of HS^- and S^{2-} ions into H_2S. The quantity of hydrogen sulphide released from the water depends on the contact time with the air (10). The remaining sulphides oxidize with the oxygen dissolved in the water into colloidal sulphur:

$$2S^{2-} + 2O_2 \rightarrow S\downarrow + SO_4^{2-}$$

which manifests itself by causing water turbidity (10, 15). Therefore, the loss of hydrogen sulphide from water and the water turbidity caused by colloidal sulphur are the consequences of water aeration. Thus, the longer water contact with the air, the greater is the loss of the sulphuric component.

Changes in sulphuric compounds due to water chlorination

The addition of chlorine, apart from inducing a loss of sulphides/hydrogen sulphide and water turbidity, also produces a substantially complex oxidizing effect on sulphides (10, 11). Oxidation may reach the insoluble elemental sulphur:

$$S^{2-} + Cl_2 \rightarrow S\downarrow + 2Cl^-$$

which causes water turbidity. At higher chlorine concentrations, sulphide oxidation may reach soluble sulphates:

$$S^{2-} + 4Cl_2 + 4H_2O \rightarrow SO_4^{2-} + 8HCl$$

but the reaction will depend on the pH of the water. For instance, up to pH 6.4 chlorine may oxidize 100 per cent of sulphides to sulphates, at about pH 7 about 70 per cent of sulphides will oxidize, and at higher pH values even lower percentages will be found. Both types of compounds may appear in the water at the same time, or may take the form of polysulphides $(HS^-)_n$ (10). As a consequence of chlorination, the water turns turbid and coloured without sulphur.

The aim of this study was to find out what causes water turbidity and change of colour and to establish the conditions under which this happens. Optimum conditions for reducing turbidity and change of colour were examined.

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WORKING METHODS

Single or hourly water samples were collected in the course of the pool's operating hours. Water temperature and residual chlorine and hydrogen sulphide concentrations were measured during sampling. Iron, manganese, nitrites, and sulphates contents as well as bacterial types, with the exception of coliform bacteria, were determined in the laboratory on the same day.

Measurements were performed in Pool 1 (200 m^3), Pool 2 (100 m^3) and in bathtubs.

The sulphuric thermal water (57 °C), which is kept in open accumulations and thus partially cooled, is poured into rehabilitation pools. The pool water temperature, from 33 to 37 °C, is reached by mixing spring water, the water from accumulations and drinking water (10). Spring water is practically clear (0.15–0.5 NTU), colourless, low in acid, with the pH between 6.6 and 6.9, alkalinity about 360 mg $CaCO_3$/L, hardness about 428, with 0.1–0.3 mg/L iron, 0.03–0.07 mg/L manganese and 5–8 m S/L total sulphides.

The pH of the sample was measured by means of an Iskra, Kranj pH-meter, MA-model number 5705. Residual chlorine was determined by the DPD (N,N diethyl-p-phenylenediamine indicator) colorimetric method (16). For iron, manganese, copper and sulphates atomic absorption was applied using a Perkin-Elmer atomic absorption spectrometer, model 305 A. Other physical and chemical tests were done with standard methods (3, 16). The number of bacteria per millilitre was determined on nutrient agar, that of coliform bacteria (most probable number MPN/100 ml) by a preliminary test on lactose broth (9), and of other bacterial types by the procedure of selective isolation from a 100 ml sample.

Reagents for chlorination: dichloroisocyanurate (Isosan-G, sodium dichloroisocyanurate dihydrate, Pliva, Zagreb, 54%-active component) and sodium hypochlorite 9.7%-active component, Polichem, Ljubljana.

RESULTS

Changes in swimming pool or bathtub thermal water samples caused by chlorination were examined and monitored at specific intervals during pool operating hours. For comparison, identical measurements were repeated in samples of non-chlorinated water. A reagent for chlorination was added to the water in the morning before the measurements started or after the first measurements in the two pools were over. Characteristic changes are shown in Figures 1, 2 and 3.

The effect of low chlorine concentration

Experiment 1. Dichloroisocyanurate, 1 mg/L, was added to Pool 1 water before the start of measurements. At the beginning of measurement a concentration of

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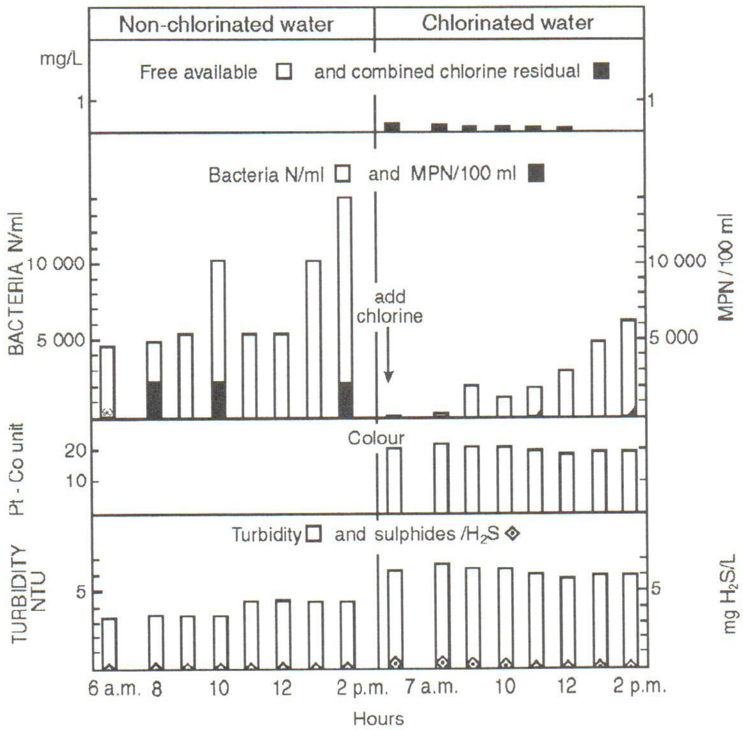

Figure 1 *Number of bacteria/ml, MPN/100 ml, colour, turbidity, and sulphides in non-chlorinated and chlorinated thermal pool water (Pool 1)*

0.2 mg/L was recorded in the form of unfavourably combined chlorine residual (CCR) which persisted at the minimum concentration of 0.05 mg/L for five hours and then disappeared (Figure 1). The number of bacteria per millilitre as a result of the effect of disinfectant and starting from a low 5/ml gradually increased because of the bathing load as the chlorine dosage, too low and in an unfavourable combination, was not sufficient to exercise a disinfecting effect with the new inflow of pollutants (18–21). There were no intestinal bacteria at the beginning of measurement but at the end of the pool operating hours *Klebsiela* and *Enterobacter aglomerans* were isolated with MPN/100 ml higher than 240. At the same time, the colour level was higher than 10 Pt-Co units and turbidity increased. Even the small quantity of 0.32 mg S/L sulphides recorded at the beginning of measurement gradually disappeared. Other parameters, measured in chlorinated and non-chlorinated water did not change to any major extent. Total hardness in non-chlorinated water was 420–433 mg $CaCO_3$/L, pH 6.88–7.00, ammonia 0.01–0.03 mg N/L, chlorides 101 mg/L and sulphates 160 mg/L.

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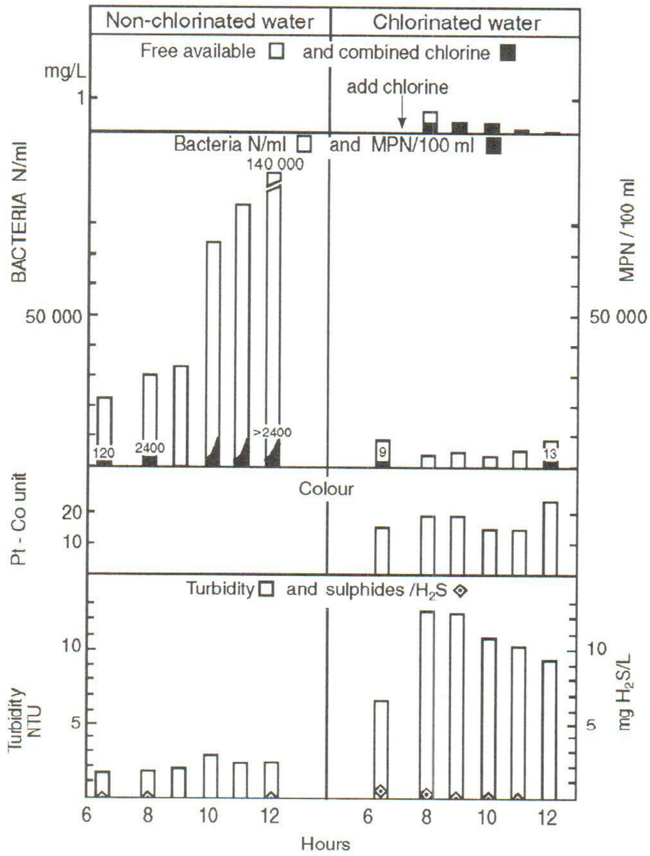

Figure 2 *Number of bacteria/ml, MPN/100 ml, colour, turbidity, and sulphides in non-chlorinated and chlorinated pool water (Pool 2)*

Experiment 2. Dichloroisocyanurate, 1 mg/L, was added after the first measurements. Differences in parameters before and after water chlorination measured in Pool 2 are shown in Figure 2. At a concentration of 0.3 mg FAC/L + 0.3 mg CCR/L the number of bacteria was reduced from 6300/ml to about 180/ml and persisted at similar values till the decrease/loss of residual chlorine in water. Afterwards, the number of bacteria per millilitre increased to about 800/ml and coliform bacteria reappeared. Like in Pool 1, a rise in colour and turbidity was registered as was disappearance of total sulphides which were 0.46 mg/L before chlorination. Likewise, the other parameters measured, i.e. hardness, chlorides, pH, sulphates, did not change after chlorination.

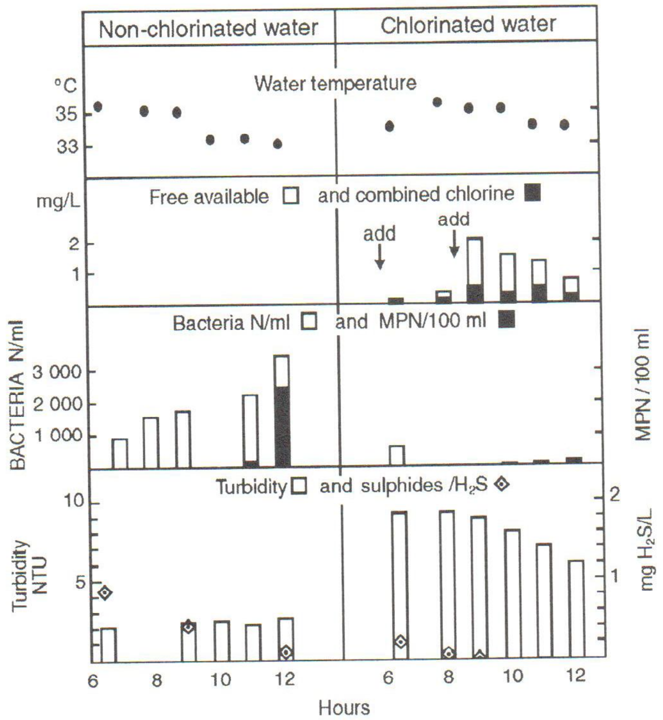

Figure 3 *Number of bacteria/ml, MPN/100 ml, colour, turbidity, sulphides and water temperature in chlorinated and non-chlorinated pool water (Pool 2)*

The effect of high chlorine concentration

Dichloroisocyanurate was added twice. It was first added at a concentration of 2.2 mg/L but was registered at 0.1 mg/L. The water became turbid and coloured. Chlorine was used up for sulphide, ammonia and iron oxidation, as was shown also in other experiments. According to *White*, 8.32 mg/L of chlorine is required to oxidize 1 mg of hydrogen sulphide to sulphate (10). However, the chlorine required to oxidize hydrogen sulphide to sulphur and water is only 2.08 mg/L chlorine to 1 mg/L hydrogen sulphide and this is the chlorine demand. After the second addition, at 2.2 mg/L, chlorine was registered at a concentration of 2.0 mg/L as total residual chlorine (TRC). Sulphides were measured at a concentration below 0.1 mg/L. With the chlorine dosage of 0.3–2 mg/L (Figure 3) the number of bacteria reached 1–2/ml, and the MPN/100 ml was lower than 2.

Figures 1, 2 and 3 show that proper chlorination, in addition to affecting bacteria, causes an unfavourable change in water colour and turbidity as well as the disappearance of sulphides/hydrogen sulphide from water.

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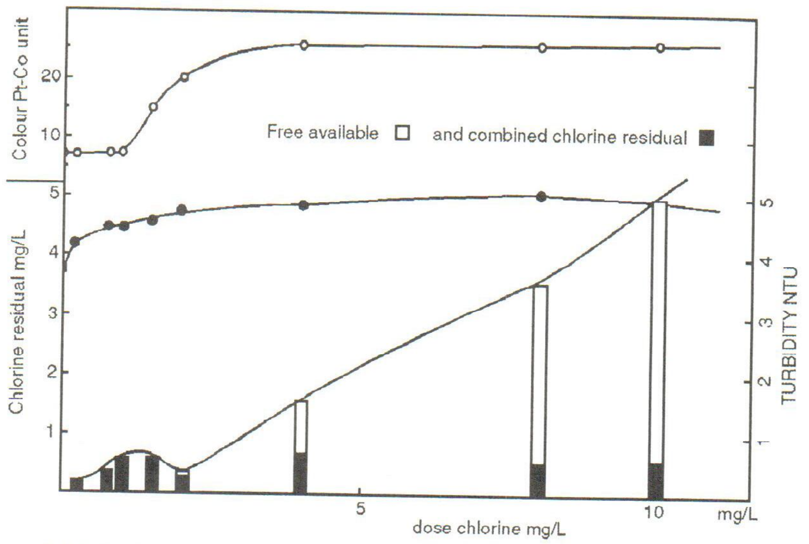

Figure 4 *Water colour and turbidity due to chlorination of thermal water under laboratory conditions*

Breakpoint chlorination

The development of water turbidity and colour caused by the addition of a chlorination reagent in laboratory conditions is shown in Figure 4. In a series of test tubes filled with thermal water at 34.2 °C, pH 7.08, ammonia 0.075 mg/L, chloride 100 mg/L, colour 7.5 Pt-Co units, turbidity 3.7 NTU, chlorine was added at a concentration of 0.2–10 mg/L. A higher concentration of residual chlorine increased first water turbidity, then colour. Owing to the presence of ammonia there is a breakpoint in the curve showing residual chlorine. The systems presented in Figure 4 were left to rest in the laboratory for two days. After two days of deposition, the settled coloured deposit dissolved in acid showed a positive reaction to iron. Chlorine also oxidizes low-valence compounds of iron and manganese into polyvalent compounds which change the water colour and together with colloidal sulphur make the situation more difficult.

The effect of chlorination with sodium hypochlorite

Additional examinations were made with another chlorination reagent, sodium hypochlorite – NaOCl, at two concentrations. Thermal sulphuric water was poured into bathtubs at a temperature of 48.5 °C. The water was left to cool to 40 °C and water colour and turbidity were measured. At first, water colour was milky

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blue and clear but then it changed to turbid. The results are presented in Tables 1 and 2.

Table 1 *Physical and chemical parameters in water before and after addition of NaOCl (Bathtub 1)*

Parameters	Before addition of NaOCl		After addition of NaOCl (in min)				
				10	35	60	90
Water temperature (°C)	48.5	37	–	36.7	36	35.6	35
Colour	bluish	turbidity		brownish	yellowish	green	
Colour Pt-Co unit	5	10	17.5	25	25	25	25
Turbidity NTU unit	4.75	12	12	12	11.5	11	11
pH	–	7.65	–	–	–	–	7.65
Free available chlorine (mg/L)	–	0	–	0.8	0.7	0.65	0.6
Combined chlorine residual (mg/L)	–	0	–	0.2	0	0	0.05
NH_3 mg N/1	–	0.225	–	–	–	–	0.1
NO_2 mgN/1	–	0	–	–	–	–	0
Sulphides mg/L	–	1.3	–	–	0.07	–	0

Table 2 *Water temperature, turbidity, colour, free and combined available chlorine residual before and after addition of low and high NaOCl concentrations (Bathtub 2)*

Parameters	Before addition of NaOCl	After addition of NaOCl (in min)				
		First addition	Second addition	95	120	150
Water temperature (°C)	38	–	–	35.3	34.5	34
Turbidity NTU unit	22.5	–	–	–	21.0	21
Colour Pt-Co scale	15	20	–	–	27.5	27.5
Colour	bluish-white	yellowish	yellowish	brownish	yellowish	green
Free available chlorine (mg/L)	0	0.80	3.0	3.0	2.0	2
Combined chlorine residual (mg/L)	0	0.2	0	0	0	0

Chlorine was added only after the water in the pool reached the usual temperature (35–36 °C), because it is known to disappear at higher temperatures (11, 17). A concentration of 0.8 mg/L NaOCl was added in bathtub 1; it was added twice in bathtub 2 until a relatively high concentration (3 mg/L) was reached. Table 2 shows that a characteristic colour appeared even when the concentration was 0.8 mg/L. The colour intensity slightly increased after a concentration of 3 mg/L of free available chlorine was reached and remained constant throughout measurement.

As seen in Tables 1 and 2, the addition of NaOCl to the thermal sulphuric water produced a change in water turbidity and colour. Those changes were independent of chlorine concentration (0.2, 0.8 or 3 mg/L).

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The effect of pH

The effect of pH on sulphide oxidation was studied in alkaline and acidic media. In one bathtub the pH of the sulphuric thermal water was adjusted to 8.2 by the addition of NaOH and in the other to 3.2 by the addition of sulphuric acid. To both bathtubs 3.0 mg/L of NaOCl or 2.5 mg/L of the chlorine preparation Isosan-G was added. The change in pH failed to affect either the colour or the turbidity.

DISCUSSION

From the point of view of hygiene, the sulphuric thermal water in this investigation was of good quality, clear and free of colour, with the characteristic high temperature of 57 °C, odour of hydrogen sulphide or sulphuric compounds (total sulphides: 5–8 mg S/L). During the technological process the thermal water is partly released into open cumulative cooling pools where it first becomes polluted and some physical and chemical changes affecting water turbidity and colour take place alongside an unfavourable bacterial situation. The total sulphide content is below 1 mg/L, the pH of the water changes from acidic to a slightly alkaline one. Due to aeration, hydrogen sulphide is partly released from water and the colloidal elemental sulphur is reduced.

The accumulation water is further transferred into therapeutic pools where it mixes with the native thermal water from the source to reach a temperature of 36 °C. The pools are non-recirculating and are emptied daily at the end of operating hours. Measurements have shown that non-chlorinated pool water is of poor bacteriological quality even before it receives a bathing load as a consequence of the water inflow from accumulations and inadequate pool cleaning. In the course of the patients' rehabilitation exercises, which last several hours in the morning, the number of bacteria per millilitre gradually rises and intestinal bacteria appear or their number is increased. The water is always slightly turbid. In all water samples total sulphides were recorded at concentrations below 1 mg/L.

If water is chlorinated and the residual chlorine dosage is not too low, the bacterial situation improves. However, water turbidity increases, the water colour changes from yellowish-red to brown, and sulphides disappear. These changes are the consequence of the complex oxidizing effect of chlorine on sulphides, as well as on iron and manganese compounds which makes the situation even more complex. The process of oxidation which started with water aeration in accumulations and continued in the pools by rapid filling-up of water and bathing load, continues even further by water chlorination and produces turbid, coloured water, free of sulphur.

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CONCLUSION

Our results show that chlorination of sulphuric thermal water should by no means be used as a method of disinfection because of the oxidizing characteristics of chlorination reagents which practically eliminate the therapeutically active sulphuric compounds from water and change the organoleptic properties of water, which becomes yellowish-brown and turbid. Reagents for chlorination cannot be replaced by any disinfectant with oxidizing characteristics (e.g. ozone, iodine, bromine).

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Sažetak

PROMJENE NEKIH KARAKTERISTIKA SUMPORNE TERMALNE VODE ZBOG KLORIRANJA

Ispitivani su negativni i pozitivni učinci kloriranja i aeracije vode u sumpornoj termalnoj vodi u bazenima za rehabilitaciju. Znatno poboljšanje mikrobiološke kvalitete vode zbog kloriranja vode dovelo je do negativnih fizikalno-kemijskih promjena vode. Zbog aeracije gubi se sumporovodik i izlučuje koloidni sumpor (mliječna mutnoća), a zbog kloriranja javlja se žućkasta, crvenkasta do smeđa obojenost ovisno o dozi klora, a također nestaju sulfidi. Kloriranje termalne sumporne vode ne bi trebalo provoditi jer se iz vode eliminiraju terapijski aktivni spojevi i dolazi do organoleptičkih promjena na koje se pacijenti žale.

Ključne riječi:
aeracija vode, doziranje klora, mutnoća, promjena boje, rehabilitacija, slobodni rezidualni klor, sumporni spojevi, voda u bazenima

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