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The Formation of Bromate During Electrolytic Generation of Chlorine (DWE 9005)

Final Report to the Department of the Environment



**THE FORMATION OF BROMATE DURING ELECTROLYTIC GENERATION
OF CHLORINE (DWE 9005)**

Final Report to the Department of the Environment

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PREFACE

The presence of bromate in drinking water is of concern since it is a suspected carcinogen. One potential source of bromate is through the use of sodium hypochlorite generated by on-site electrolysis of brine. Few data exist on the concentration of bromate either in hypochlorite solutions generated on-site, or in the corresponding final waters.

The Department of the Environment placed a contract with WRc to review the theoretical basis for the formation of bromate during the electrolysis of sodium chloride, to assess the potential yield of bromate in hypochlorite solutions, to relate this to possible concentrations in treated waters and to determine the concentration of bromate in hypochlorite solutions and the associated treated waters taken from sites using on-site electrolytic systems.

This final report presents the work undertaken.

SUMMARY

The use of ozone in drinking water treatment has led to concern about the possible formation of harmful by-products. Of particular concern is bromate, which can be formed from the ozonation of raw waters containing bromide. Bromate is a suspected carcinogen and is included in the revised WHO Guidelines for drinking water. The WHO have set a provisional guideline value of $25 \mu\text{g l}^{-1}$, taking account of perceived analytical problems associated with the determination of bromate in drinking water. However, in the absence of such problems the low dose extrapolation models commonly used when deriving guideline values give a value of $3 \mu\text{g l}^{-1}$.

Another potential source of bromate is the use of sodium hypochlorite (either generated on-site or commercially available). There is a growing interest in the use of on-site electrolytically-generated chlorine for water treatment but brine used in on-site generators will contain bromide, and it is possible that it will be oxidised, leading to bromate in the treated water. There are few data on the levels of bromate either in hypochlorite solutions generated on-site or in the associated final waters.

The objectives of this study were threefold:

- review the theoretical basis for the formation of bromate during the electrolysis of sodium chloride;
- to assess the potential yield of bromate in the hypochlorite solution produced by on-site electrolytic systems and relate this to possible concentrations in treated waters;
- to determine the concentration of bromate in hypochlorite solutions and the associated treated waters, taken from sites using on-site electrolytic systems.

The work showed that bromate is formed during on-site generation of hypochlorite. The concentrations found in hypochlorite samples ranged from 2.8 to 21.8 mg l^{-1} . However, bromate was only found in two out of twelve final waters analysed. These corresponded to the two hypochlorite solutions containing the highest concentrations of bromate. It appears unlikely that the provisional WHO Guideline for bromate of $25 \mu\text{g l}^{-1}$ would be exceeded through the use of on-site generated hypochlorite alone. If a lower value (i.e. less than $10 \mu\text{g l}^{-1}$) were adopted then it is feasible that exceedances could occur at some sites. A major factor determining the level of bromate present in hypochlorite will be the bromide concentration in the brine. This will depend on the bromide content of the salt and the strength of the brine. The brine strength is likely to vary significantly in different systems. In some cases it is increased to maintain a pre-determined hypochlorite concentration in the outlet stream (normally 0.7-0.9% chlorine).

Other operating conditions could affect the amount of bromide converted to bromate. These include cell voltage, current density, operating temperature and residence time in the generator cell. To a certain extent all these parameters are inter-related, and whilst it is difficult to predict the effect of changes in any one of them on bromate production, it is possible that any increase in one or other parameter is likely to favour bromate production.

Storage of on-site generated hypochlorite does not seem to result in significant increases in bromate concentrations.

The type of on-site generating system does not appear to be important in determining the level of bromate formed.

The significance of the findings clearly depends on the numerical value of any standard set for drinking water. However, some further investigations would seem prudent.

Wider monitoring of bromate concentrations in hypochlorite solutions generated by on-site systems, and of bromide concentrations in brines should be carried out.

Since it is not possible to explain the reason for the two detected levels of bromate in treated water, due to insufficient data on the brine feedstocks and detailed operating conditions, a detailed study of the factors that control bromate formation should be carried out. In practice, this would require a test rig to allow bromate monitoring under the full range of operating conditions.

1. INTRODUCTION

The increase in recent years in the use of ozone in drinking water treatment has led to concern about the possible formation of harmful by-products. Of particular concern is bromate, which can be formed from the ozonation of raw waters containing bromide. Bromate is a suspected carcinogen and is included in the revised WHO Guidelines for drinking water. The WHO have set a provisional guideline value of $25 \mu\text{g l}^{-1}$, taking account of some of the analytical problems associated with the low level determination of bromate in drinking water. In the absence of analytical problems a guideline value of $3 \mu\text{g l}^{-1}$ would be proposed on the basis of an additional cancer risk of 1 per 100 000 population in 70 years.

Although it is the interest in the use of ozone that has highlighted the potential problem with bromate formation, another potential source of bromate is through the use of sodium hypochlorite (either generated on-site or commercially available). There is a growing interest in the use of on-site electrolytically-generated chlorine for water treatment, in the main because it would reduce the need for bulk delivery of hazardous chemicals (either chlorine gas or sodium hypochlorite solution). The brine used in on-site generators will inevitably contain small amounts of bromide, and under the conditions used to generate chlorine from chloride it is possible that bromide will be oxidised to bromate, and that low levels of bromate could end up in the treated water. There are very few data on the levels of bromate either in hypochlorite solutions generated on-site or in the associated final waters.

The objectives of this study were to:

- review the theoretical basis for the formation of bromate during the electrolysis of sodium chloride;
- assess the potential yield of bromate in the hypochlorite solution produced by on-site electrolytic systems, and relate this to possible concentrations in treated waters;
- determine the concentration of bromate in hypochlorite solutions and the associated treated waters, taken from sites using on-site electrolytic systems.

2. BROMATE FORMATION DURING ELECTROLYTIC GENERATION OF CHLORINE

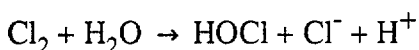
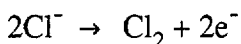
2.1 Basis of electrolytic generation of chlorine

The basis of the production of chlorine, or sodium hypochlorite, is the electrolysis of brine (aqueous sodium chloride). Softened water is passed through a salt saturator and the resultant brine stream diluted further to give the desired brine concentration (typically around 30 g l^{-1}). The brine is then passed through an electrolysis cell, resulting in the production of chlorine, hydrogen and sodium hydroxide. Four types of electrolysis cells have been used for this purpose:

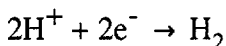
- (a) Mercury cells
- (b) Diaphragm cells
- (c) Membrane cells
- (d) Undivided cells

The first two types will not be discussed further, since they are not used in any of the on-site systems currently available. It is believed that all the on-site generators used in drinking water treatment in the UK use undivided cells, but it is possible that there are a few units that use membrane cells. The basic electrochemistry taking place in an undivided cell can be summarised as follows:

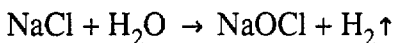
Anode:



Cathode:



Net reaction:



Hence, the overall process can be regarded as the electrolysis of aqueous sodium chloride to produce aqueous sodium hypochlorite and hydrogen gas. The key difference between membrane cells and undivided cells is that in the membrane cell the anode and the cathode are separated by a semi-permeable membrane, which allows only a severely restricted flow of anions across it (whereas the undivided cells have no barrier). The practical implication of this difference is that whereas the output stream of an undivided cell is a solution of sodium hypochlorite - i.e. the chlorine (from the anode) and the sodium hydroxide (from the cathode) react together - a membrane cell produces two

streams, one of dissolved chlorine and one of sodium hydroxide, which are subsequently blended to produce a solution of sodium hypochlorite. In both cases the final hypochlorite solution has a pH of about 9.

The anodes of the cell, DSA or Dimensionally Stable Anodes, are typically made of titanium, titanium coated with a metal oxide layer (either a single metal, e.g. ruthenium or a mixture) or platinum. The cathodes are typically made of titanium or 'Hastelloy' (a series of nickel-based alloys), although steel is also used. During electrolysis the pH at the cathode surface will be highly alkaline due to the high residual concentration of hydroxide ion after hydrogen evolution. The relatively high pH environment will tend to lead to the precipitation of calcium (as carbonate) and magnesium (as hydroxide) and thus, in order to reduce problems with electrode scaling, the water is softened by ion exchange resin prior to use.

The electrolysis process will significantly increase the temperature of the electrolyte, and therefore the output from the cell is passed through a heat exchanger, with the heat being used to warm the influent to the cell to within the specified operating temperature range (typically 7-30°C). If the temperature falls below this range then the cell conductivity drops below an acceptable level.

The output of the generator cell is passed into a holding tank, which will typically hold sufficient sodium hypochlorite for 24-36 hours operation. Dosing pumps are then used to control the addition of the correct amount of hypochlorite to the water during treatment.

2.2 Formation of bromate

2.2.1 Source of bromate

The sodium chloride used in the electrolytic generation of chlorine will inevitably contain small amounts of bromide. Under the conditions used in on-site hypochlorite generation, two possible mechanisms exist for the formation of bromate from the bromide present in the inlet brine solution:

Electrolysis of bromide

From the electrode potentials shown in Figure 2.1, it is apparent that under the alkaline conditions that result from the production of chlorine from chloride, the electrolysis of bromide to form bromate will be highly thermodynamically favourable. Whilst it is difficult to comment on the kinetics of the process, it is likely that a proportion of any bromide present will be electrolysed to yield bromate.

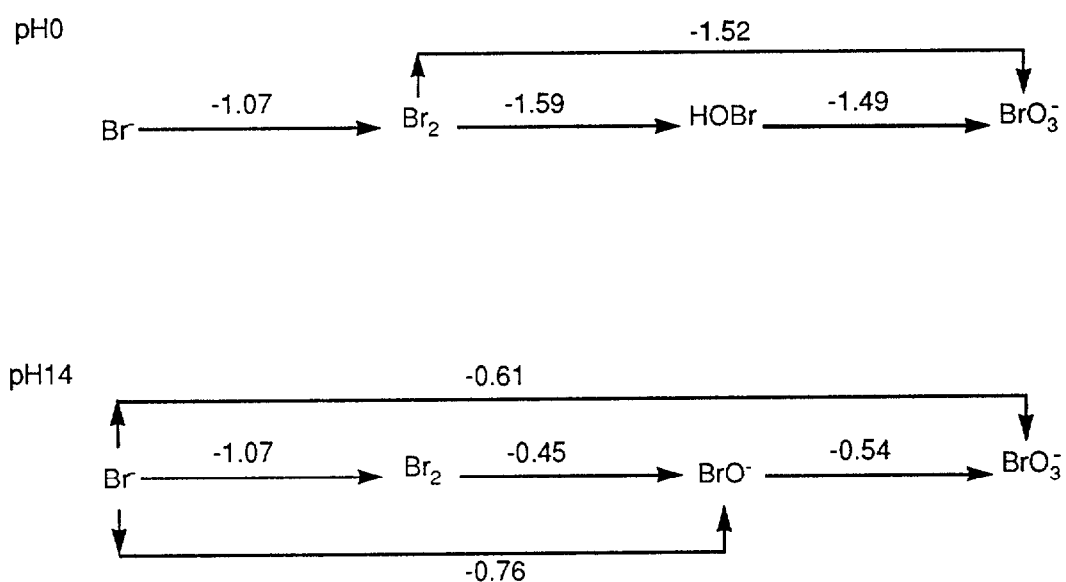


Figure 2.1 Standard electrode potentials (v) for anode reactions of bromine species under acidic and basic conditions

Oxidation of bromide by chlorine

Bromide can, under certain conditions, be oxidised by chlorine to bromine and bromate, and it is possible that this reaction could occur in the bulk electrolyte. In addition, since a certain amount of the brine will pass through the generator cell unreacted, further oxidation of any residual bromide could take place in the storage tank.

Bromate, formed by either of the mechanisms described above, may therefore be present as an impurity in on-site generated hypochlorite. Hence, the use of hypochlorite in drinking water disinfection could result in the addition of small amounts of bromate to the treated waters.

2.2.2 Potential levels of bromate

Prior to the work carried out during this study (Section 2.3), there were very few data on the concentration of bromate in either the generated hypochlorite or final water disinfected with hypochlorite generated on-site. A few results obtained recently indicate that bromate is present in on-site generated hypochlorite, but that detectable concentrations ($\geq 2 \mu\text{g l}^{-1}$) are not found in the corresponding final waters (WRc Report DoE 3397). Data recently published on the concentration of bromate in commercial hypochlorite solutions indicate that bromate is present as a contaminant of hypochlorite (Bolyard *et al.* 1992). The levels found varied and no indication was given whether the bromate arose from the manufacture or storage of the hypochlorite solution. No bromate was detected in any of the final waters analysed in the Bolyard study.

A maximum theoretical concentration of bromate in on-site generated hypochlorite can be calculated by assuming that all the bromide present in the brine is oxidised to bromate, and that the generator cell is operating under typical operating conditions. The bromide content of commercially-available salt can vary greatly (between 100 and 350 ppm as bromide in sodium chloride, i.e. a chlorine:bromine ratio of between 1800:1 and 6000:1). Assuming a chlorine:bromine ratio of 1800:1, the following calculations can be made:

Brine concentration	3% w/v NaCl solution
Concentration of bromide in brine	10.5 mg l^{-1}
Maximum bromate concentration in effluent	17 mg l^{-1}

Most on-site generators are designed to deliver a concentration in the outlet stream of between 0.7 and 0.9% chlorine. During this study the information obtained indicated that in practice hypochlorite strengths of 0.7-0.75% were usual. Assuming an average value of 0.8%, then for a chlorine dose of 1 mg l^{-1} the maximum bromate concentration in the final water will be $2 \mu\text{g l}^{-1}$. Clearly, the use of higher chlorine doses will lead to a correspondingly greater concentration of bromate in the final water.

2.3 Bromate survey

As indicated above, data on the concentration of bromate in hypochlorite solutions produced by on-site systems is scarce. A survey was undertaken to provide data on the levels of bromate both in the hypochlorite solutions and in the corresponding final waters. Five systems for electrolytic production of sodium hypochlorite are included in the 1992 Secretary of State's List of Approved Substances:

- | | |
|-----------------------------|-----------------------------------|
| 1. Capital Controls | - ElectroCell Process |
| 2. Electrocatalytic | - Pacpuri System |
| 3. Stella-Meta Filters Ltd. | - Clorocel Hypochlorite Generator |
| 4. Wallace and Tiernan Ltd. | - OSEC System |
| 5. Wyted (Kempsey) Ltd. | - Wyted Electrolytic Process |

It was originally intended to sample from sites using the different systems. However, enquiries revealed that Wyted (Kempsey) Ltd has recently been bought by Stella-Meta Filters Ltd. (SMF) and it was suspected that no Wyted systems were currently in use. Furthermore, after discussions with Capital Controls, no site using the ElectroCell process could be located. Wallace and Tiernan's OSEC system is the most widely used, followed by Electrocatalytic's Pacpuri system, and this is reflected in the sites sampled. One site using a SMF Clorocel generator was identified and sampled.

Samples of hypochlorite were taken at each site from the storage tank, together with samples of raw and final water. The hypochlorite samples were diluted either 100 or 1000 times to bring them into the working range of the ion chromatograph. The results are given in Table 2.1. Repeat analyses of the hypochlorite solutions were carried out after 2-3 weeks storage (at ambient temperature).

Table 2.1 Bromate concentrations in hypochlorite, raw and final waters taken from treatment works using on-site electrolytically-generated chlorine

Site	System	Bromate concentration in hypochlorite (mg l ⁻¹)		Chlorine dose (mg l ⁻¹)	Bromate concentration (µg l ⁻¹)	
		Pre-storage ^a	Post storage ^b		Raw water	Final water
A	OSEC	3.6	3.2	2.1	<2	<2
B	OSEC	3.9	4.0	2.3	<2	<2
C	SMF	5.2	nd	1.2	<2	<2
D	Pacpuri	21.8	nd	0.7	<2	2
E	OSEC	14.2	nd	2.5	<2	5
F	OSEC	3.5	3.6	2.0	<2	<2
G	Pacpuri	8.3	9.4	na	<2	<2
H	Pacpuri	2.8	3.4	0.7	<2	<2
I	MicroOSEC	3.4	4.8	1.0	<2	<2
J	Pacpuri	9.3	9.8	na	<2	<2
K	Pacpuri	8.7	12.0	na	<2	<2
L	OSEC	2.8	3.2	na	<2	<2

Notes: ^a Samples analysed on collection

^b Repeat analysis after 2-3 weeks storage at ambient temperature

nd = not determined

na = data not available

It is clear from Table 2.1 that bromate is formed during the on-site generation of hypochlorite, the amount formed ranging from 2.8 and 21.8 mg l⁻¹. Bromate was detected in only two of the final waters analysed, corresponding to those disinfected with hypochlorite containing the highest bromate levels (Sites D and E). Where chlorine data are available, the measured bromate levels in the final waters agree very well with calculated values based on the bromate concentration determined in the hypochlorite solution. For example, at Site E:

Bromate concentration in hypochlorite:	14.2 mg l ⁻¹
Hypochlorite strength (as Cl):	7.5 g l ⁻¹
Chlorine dose:	2.5 mg l ⁻¹
Calculated bromate concentration in final water:	4.7 µg l ⁻¹
Measured bromate concentration:	5 µg l ⁻¹

The reasons for the wide variation of bromate concentrations in the generated hypochlorite are unclear. However, several factors are likely to affect the amount of bromate formed during the electrolytic process. Of these, the concentration of bromide in the brine is likely to be the most important. Variation in the bromide content of the salt and in the ionic strength of the brine solution used will both affect the concentration of bromide in the brine solution. The salt required to generate 1 kg of chlorine will depend on feedwater and salt quality, and on temperature - Wallace and Tiernan quote a range of 3.0 to 3.9 kg in their promotional literature. On-site systems are usually run to produce a constant strength of hypochlorite (0.7-0.9% as chlorine) and changes in temperature or feedwater quality may mean a higher salt requirement to maintain the hypochlorite strength. Clearly a system operating with a higher ionic strength brine will have the potential to produce more bromate. Loss of efficiency (for example caused by electrode deterioration) is often compensated for by increased brine strength.

It is difficult to predict the effect of other operational parameters on likely bromate production. The design of the cells for the three systems sampled is very similar, and it seems unlikely that one or other system will be more susceptible to bromate formation (a view supported by the range of results obtained during this study). Other factors that could affect bromate production include cell voltage, current density, operating temperature, residence time within the generator cell and state of the electrodes. To a greater or lesser extent, most of these parameters are inter-related. In general, systems are likely to be run so as to maintain a constant concentration of hypochlorite and it is possible that measures taken to overcome any loss in efficiency, such as increasing cell voltage or brine strength (see above), could cause an increase in bromate formation.

Storage of the hypochlorite solutions did not have a great effect on the bromate levels. Some samples showed a slight increase, which could be caused by the oxidation of any bromide remaining by chlorine. It seems, however, that this reaction is very slow compared to the electrolysis of bromide to form bromate, and its storage is therefore unlikely to result in substantially more bromate formation. In practice, the generated hypochlorite is likely to be used within 48 hours, and is very unlikely to be stored for longer than a week (compared to the 2-3 weeks that the samples were in this study).

The results from the analysis of final waters taken from works using on-site generated hypochlorite suggest that bromate will only occasionally be found at concentrations above the current detection limit ($2 \mu\text{g l}^{-1}$). In the majority of cases it, therefore, seems extremely unlikely that the provisional WHO guideline value for bromate of $25 \mu\text{g l}^{-1}$ will be exceeded through the use of on-site generated hypochlorite alone. However, were a lower value adopted (e.g. $\leq 10 \mu\text{g l}^{-1}$), then exceedances could occur (e.g. in a works using an on-site system generating 20 mg l^{-1} bromate, dosing at 5 mg l^{-1} chlorine, the bromate level in the final water could be as high as $13 \mu\text{g l}^{-1}$). An additional consideration, is in relation to the use of final chlorination after ozonation, where the combined bromate concentrations arising from each process might prove significant.

3. CONCLUSIONS AND RECOMMENDATIONS

The main conclusions from this study, concerning the production of bromate through the use of on-site electrolytic generation of chlorine, can be summarised as follows:

1. Bromate is formed during on-site generation of hypochlorite. The concentrations found in hypochlorite samples ranged from 2.8 to 21.8 mg l⁻¹. The upper end of this range exceeds the theoretical maximum (calculated by assuming all the bromide likely to be present in the brine solution is converted to bromate), probably because the brine concentration is higher than the usual upper level of 3% w/v NaCl.
2. Detectable concentrations of bromate were found in two final waters analysed. These corresponded to the two hypochlorite solutions containing the highest concentrations of bromate. The concentration of bromate present in a particular final water will be a function of the concentration in the hypochlorite and the chlorine dose.
3. It is very unlikely that the provisional WHO Guideline for bromate of 25 µg l⁻¹ would be exceeded through the use of on-site generated hypochlorite alone. If a lower value (e.g. ≤ 10 µg l⁻¹) is adopted, then it is feasible that exceedances could occur.
4. A major factor in determining the level of bromate present in hypochlorite is likely to be the bromide concentration in the brine entering the generator cell. This will be determined by a combination of the original bromide content of the salt and the ionic strength of the brine. The brine strength is likely to vary significantly in different systems, and in some cases it is increased to maintain a pre-determined hypochlorite concentration in the outlet stream (normally 0.7-0.9% chlorine).
5. Other variations in operating procedures could affect the amount of bromide converted to bromate. These include cell voltage, current density, operating temperature and residence time in the generator cell. To a certain extent all these parameters will be inter-related, and whilst it is difficult to predict the effect of changes in any one of them on bromate production, it is likely that any increase in one or other parameter is likely to favour bromate production.
6. Loss of efficiency, possibly through deterioration of the electrode surface or poor feed water quality, may be overcome through an increase in cell voltage, which is likely to result in more bromate formation. Increasing brine concentration is another option.
7. Storage of on-site generated hypochlorite does not seem to result in significant increase in bromate concentrations, suggesting that the majority of the bromate is formed through electrolysis of bromide, rather than oxidation by chlorine (either in the generator cell or in the storage tank).
8. The type of on-site generating system does not seem to be important in determining the level of bromate formed. Three systems were sampled during this study, but no one type was found to produce more bromate than the others. All the systems

sampled are based on essentially the same cell design (similar electrodes etc.) and operate under broadly similar conditions. Any variations in bromate production due to slight variations in cell design are likely to be outweighed by other variations (e.g. brine strength, cell voltage).

Arising from the above, a number of recommendations can be made:

1. Wider monitoring of bromate concentrations in hypochlorite solutions generated by on-site systems, and of bromide concentrations in brines should be carried out. This would serve two purposes:
 - to identify systems generating high levels of bromate and, by relating this to the chlorine dose used, sites where bromate concentrations in the final water are likely to be $\geq 2 \mu\text{g l}^{-1}$ and whether moving to salt supplies with lower bromide contents may significantly reduce bromate concentrations;
 - to highlight systems where bromate production was increasing over a period of time (possibly due to increase in brine strength or cell voltage to compensate for a drop in efficiency).
2. Periodic checks of the inlet brine concentration should be carried out to ensure that the system is operating within the specified range. An unnecessarily high brine strength will have cost implications as well as possibly resulting in higher bromate concentrations in the hypochlorite solution.
3. A detailed study of the factors that affect the extent of bromate formation during the generation of hypochlorite should be carried out. In practice, this would require a test rig to allow bromate production to be monitored under the full range of operating conditions.