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Measurement of Produced Water Discharges – Regulatory Requirements and Recent Progress

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1 INTRODUCTION

Until recently, produced water was considered to be a waste stream for which metering was not a critical issue. As a result, little attention had been paid to the subject of metering this stream. However, in 2001 OSPAR (Oslo – Paris Commission) recommended a 15% reduction of oil discharged via produced water by 2006 [1], in relation to the year 2000. This meant that there was a need to accurately measure both the concentration of oil in produced water and the volume of water being discharged. In the UK, new Regulations, called OPPC (Offshore Pollution Prevention and Control) [2] were introduced in 2005, which require the measurement of produced water volume to an uncertainty of ± 10% [3].

This paper is divided into two parts. The first part (Part A) will provide a summary of the regulatory requirements related to the discharge of produced water in the North Sea and in UK in particular. It will examine the measurement issues raised by the introduction of the new legislation, including the best methods of achieving the performance targets. The second part (Part B) illustrates the importance of reporting produced water volumes at standard conditions of temperature and pressure (15°C and 1.01325 bar absolute). Equations that can be used to calculate the density, and hence the expansion factors of produced water are proposed. These apply across the wide range of temperatures and salinities found in practice.

PART A: REGULATORY REQUIREMENTS AND RECENT PROGRESS

2 REGULATORY REQUIREMENTS

International Law considers five main categories of discharges associated with the operations of offshore platforms. These are [4]:

- Platform drainage from machinery spaces, e.g. pumps and generator areas
- Contaminated sea water due to normal operations, e.g. storage tanks cleaning
- Offshore processing drainage, e.g. leaks collected from treatment installations and surface piping
- Production water, i.e. the water separated from production fluids
- Displacement water, i.e. water used to compensate the decreasing level of oil in storage tanks to assist offloading and to ensure stability and integrity of the platforms

The first two of these are regulated under the provision of the International Convention for the Prevention of Pollution from Ships 1973, as amended 1978 (MARPOL 73/78) [5]. Annex I of MARPOL 73/78 provides the full regulations for the prevention of pollution by oil, which entered into force on 2 October 1983. Here

one of the key points is that the water must be treated and can only be discharged if the concentration of the oil is less than 15 parts per million (volume/volume) or ppm.

The discharges associated with the other three categories are regulated through national and regional regulations.

As oil fields mature, increasing amounts of water are being produced. Worldwide it is estimated some 250 million barrels are produced daily [6], which is more than three times the amount of oil produced. In the North Sea, some 9 million barrels per day is produced of which some 15% is re-injected [7]. As a result, around 8547 tonnes of oil (OSPAR 2004 official figure) is discharged via the discharge of produced water in the North Sea. Produced water is by far the largest waste stream for oil production. Oil discharged via the discharge of produced water now accounts for over 90% of the total amount of oil discharged to the sea in the North Sea as figures shown in Table 1.

Table 1 Amount of oil discharged into the North Sea in 2004 [7]

Source of oil discharged	Produced & displacement water	Oil and organic fluids from drilling	Oil spillage	Total
Quantity (tonnes)	8547	425	199	9171
Percentage (%)	93.2	4.6	2.2	100

Produced water also contains components such as heavy metals, production chemicals and naturally occurring radioactive materials (NORM) in addition to the residual oil. Therefore its discharge is in general strictly regulated as these components can potentially cause damage to the marine environment.

2.1 Regulatory Framework in the North Sea

In the North Sea, OSPAR was created to look after the marine environment. It is a convention which is legally binding on its member states ("contracting parties") with an area that encompasses the North East Atlantic from Greenland down to the Straits of Gibraltar.

OSPAR was created when Oslo Convention and Paris Convention was merged in 1992. It came into force on 25 March 1998. The Oslo Convention was originally created for the prevention of marine pollution by dumping from ships and aircraft, which was signed in 1972 in Oslo. The Paris Convention was made for the prevention of marine pollution from land-based sources, which was signed in 1974 in Paris.

OSPAR takes three types of measures, termed decisions, recommendations and agreements. Decisions are formal and legally binding on the contracting parties. Recommendations are not legally binding, but still formal and usually most contracting parties implement these in the same way as the decisions. Decisions and recommendations from OSPAR are made to address specific issues that are essential to reach the objectives of OSPAR. Less important measures, which may be addressed

by less formal agreements, come under the category of "other agreements". Agreements are not legally binding.

Implementation of OSPAR measures can be made in three ways: enforcement by law, implementation by administrative action or by negotiated agreement between the competent authorities and industry.

One of the key measures undertaken by OSPAR recently is the OSPAR Recommendation 2001/1 for the Management of Produced Water from Offshore Installations [1], which was adopted in June 2001. The Recommendation has since been amended in 2006 [8]. Some of the key points included in the recommendation are:

- Any new or substantially modified existing installation after 1st January 2002 must take, as a point of departure, zero discharge of oil in produced water into the sea or at least the minimisation of discharges.
- Each contracting party has to make a complete review of existing installations, of Best Available Technology (BAT) and Best Environment Practical (BEP) used for the management of produced water, by the end of 2005.
- For each contracting party, the total quantity of oil in produced water discharged into the sea during the year 2006 from all installations must be reduced by a minimum of 15% compared to the equivalent discharge in the year of 2000.
- The performance standard for dispersed hydrocarbons in the discharged water is reduced from 40 mg/l to 30 mg/l by the end of 2006.
- The dispersed oil content in the produced water should be measured using an infrared method as adopted in 1988, as described by the Agreement 97-16 [9].

The update of the recommendation in 2006 reflects the changes made since the recommendation was originally produced. The main points are:

- No individual offshore installation should exceed a performance standard for dispersed oil of 30 mg/l from 1 January 2007.
- Contracting parties should report to the OSPAR Offshore Industry Committee (OIC) meeting in 2008 the offshore installations that fail to meet the performance standard of 30 mg/l.
- Contracting parties should continue to exchange information on dissolved oil in produced water on the basis of work in hand.
- The new reference method for the measurement of dispersed oil against which the performance standard is set is the method described in OSPAR Agreement 2005-15 [10].

Until the OSPAR Recommendation 2001/1, the only parameter, with which a performance standard was set, was the dispersed oil concentration. Presently, oil in produced water concentration is still the main parameter that is measured and compared to the performance standard for compliance.

However in the OSPAR Recommendation 2001/1, not only the performance standard was lowered from 40 mg/l to 30 mg/l, but also each contracting party was required to

make a minimum of 15% reduction in the amount of oil discharged into the sea via the discharge of produced water by the year 2006 compared to the year 2000 figure. As a result, accurate measurement of oil concentration was no longer the only thing that operators have to comply with. Accurate quantification of the discharge volume and meeting the overall 15% reduction had become equally important.

2.2 Regulatory Framework in UK

The discharge of produced water in the United Kingdom Continental Shelf (UKCS) is regulated by the Department of Business, Enterprise and Regulatory Reforms (BERR), formerly called the Department of Trade and Industry (DTI). In the past, the key piece of legislation was the Prevention of Oil Pollution Act 1971 (PoPA). However PoPA has now been replaced by OPPC Regulations 2005, which came into force in August 2005. The new Regulations have been designed to encourage offshore operators to continue to reduce the quantities of hydrocarbons discharged during the course of offshore operations. The Regulations updated the definition of oil, introduced a permitting system for oil discharges and strengthened BERR's powers to inspect and investigate oil discharges. The issue of permits under these new regulations has replaced the issue of exemptions under the previous Regulations and will be on a permanent basis for the duration of an activity covered. These new Regulations were made in line with the OSPAR Recommendation 2001/1.

To facilitate the attainment of the 15% reduction target in oil discharges from 2000, a Produced Water Trading Scheme has been set up in the UK. In this Scheme, which started on 1 January 2007, permits are issued to each installation in the UKCS that discharges produced water. The permits are issued according to an allocation plan, which gives details of discharge allowances for each installation. Discharge allowances allocated by BERR are the maximum amount of dispersed oil that is permitted to be discharged by an installation.

Allowances can then be traded to achieve compliance. The Trading Scheme in UK was designed to provide a mechanism in which the 15% reduction target could be achieved in a cost-effective way. It also provides the means to achieve further oil discharge reductions in the future.

2.2.1 Measurement of Dispersed Oil in Produced Water

(i) Performance standard

The OPPC Regulations prohibit the discharge of oil into the sea unless it is in accordance with the schedule conditions of a permit issued to cover the discharge. Many of the schedule conditions contained in an OPPC permit depend on the accurate measurement of oil. On 1 January 2006 the performance standard for dispersed hydrocarbons in the UKCS was reduced from 40 mg/l to 30 mg/l, which was a year earlier than the OSPAR Recommendation 2001/1 required.

(ii) Approved analysis methods

Until the end of 2006, the only oil-in-water analysis method approved by BERR was the infrared (IR) / tetrachloroethylene (TTCE) method (BERR IR method) [11]. Since 1 January 2007 the new OSPAR/(BERR) approved oil-in-water analysis reference method is the OSPAR GC-FID method [10].

(iii) Sampling

Details of oil in produced water sampling requirements can be found in the BERR Guidance notes [12]. A brief summary is provided here.

If an installation discharges more than 2 tonnes of dispersed oil per annum, for manned installations, a minimum of 2 samples should be taken at an approximately equal time intervals. For unmanned installations, three duplicate samples are taken each time the installation is visited, one is analysed and reported. Providing that the result obtained is satisfactory the other two are discarded. When the installation is temporally manned for more than 48 hours, one sample is taken every 48 hours.

If the installation discharges less than two tonnes per annum, for manned installations, three duplicate samples are taken once a month. One is analysed and reported; if the result is satisfactory the other two are discarded. If the installations are unmanned, then three duplicate samples are taken each time the installation is visited unless the visit is repeated in the calendar month. One is analysed and reported. Providing the result obtained is satisfactory the other two are discarded.

For installations that discharge produced water in batches, representative sample(s) of each batch must be taken and analysed.

2.2.2 Measurement of Produced Water Discharges

(i) Performance standard

An early version of the BERR guidance notes [13] issued in 2004 on OPPC Regulations stated that permit holders should monitor or calculate the volume of the produced water discharge to ± 10% uncertainty on volume. Although not stated explicitly, this refers to a 95% confidence level. It also stated that the discharge volume should be determined daily and the volume reported at standard conditions (15°C and 1.01325 bar).

The current permit schedule as shown on the BERR website [3] requires the following:

"Details of the method used to measure the volume discharged, or the method used to calculate (or estimate) the average daily production of the discharge stream (this should include an estimate of the uncertainty of the measurement or calculation, e.g. +/- 10% for this produced water discharges). It should be noted that the method of measurement may require to be independently verified, as a condition of the oil discharge permit"

There is currently no reference to the need to express the discharge volume at standard conditions.

(ii) Measurement methods

The most popular method employed to quantify produced water discharges is direct metering. This method has the lowest uncertainty and is most likely to attain the performance target stipulated in the previous section. Other methods employed include estimation of volume using well test data or inference of flow from pressure drops across hydrocyclones. In this area there are still several issues to be considered such as how the measurement methods should be verified or calibrated and whether current measurement methods could be used to derive reliable data for individual assets served by the same host discharging installation. However there is no standard or reference method for produced water volume determination.

2.2.3 Reporting of Produced Water Discharges

Permit holders are currently required to maintain detailed records of the sampling and analyses undertaken, and the quantities of produced water discharged. BERR has the legal right to view those records, but the normal method of accessing the dispersed oil in produced water discharge data is via the EEMS (Environmental Emissions Monitoring Service) database [14].

(i) Oil-in-Water discharge report

Submission of the EEMS database returns will continue to be a condition of permits issued under the OPPC Regulations, and permit holders will be required to submit the returns on a calendar monthly basis, supplemented by an annual summary return. These returns will continue to be used to assess compliance with legislative reporting requirements. BERR may additionally request access to the original records to check the EEMS data.

(ii) Operator report

This is a record that should be retained by the operator and, according to BERR OPPC guidance notes, should include the following:

- The date and time when the oil-in-water samples were collected
- The hydrocarbon concentration of each sample
- The volume of the daily discharge
- The daily hydrocarbon discharge
- The monthly hydrocarbon discharge
- The volume of the annual discharge
- The annual hydrocarbon discharge

(iii) New reporting requirements

In addition to the EEMS reporting requirements, since 1 January 2007 a new condition was included in the permits issued under the OPPC Regulations, requiring

permit holders to prepare a separate, annual, Dispersed Oil in Produced Water Trading Scheme Discharge Report, and to seek independent verification of that report to demonstrate compliance with the Rules of the Scheme.

This report should include the following information

- The analyses and measurements undertaken to quantify discharges of dispersed oil in produced water
- The methodologies employed for the analyses and measurements
- The uncertainties associated with the analyses and measurements
- The methodology used to calculate the quantity of dispersed oil in produced water during each calendar year

A new guidance (draft version) on how to prepare this report has recently been released by BERR [15].

2.2.4 Annual Discharge Report Verification

Permit holders must instruct accredited verifiers to audit and review the annual report and to verify the quantity of dispersed oil in produced water during each calendar year. The verification should be undertaken in accordance with the requirements specified by BERR, and the verified report must be submitted to BERR no later than 30 April of the year following the calendar year to which the report relates.

Verification must be carried out by an independent organisation which is UKAS (United Kingdom Accreditation Service) accredited. The objective of the verification exercise is to establish that clear evidence exists to demonstrate how the annual discharge oil in produced water figure is derived, and that this figure is accurate.

Verifiers will however in general not be required to go offshore in order to complete the verification.

At the previous North Sea Flow Measurement Workshop, Beecroft [18] provided a comprehensive review of the history of regulations related to the discharge of produced water from offshore installations with a particular emphasis on the United Kingdom sector.

3 RECENT PROGRESS

In anticipation of the implementation of the OSPAR Recommendation 2001/1, in particular regarding the introduction of a new oil-in-water analysis reference method, and the 15% discharge oil reduction target, two Joint Industry Projects (JIP) were subsequently launched by TUV NEL – Oil-in-water Analysis Method (OIWAM) and Produced Water Volume Determination (ProVol).

3.1 Oil-in-water Analysis Method (OIWAM)

Following the OSPAR 2001/1 Recommendation and subsequent agreement to adopt a new reference oil-in-water analysis method based on using gas chromatograph, it soon became clear that the offshore oil and gas industry would face some major challenges in implementing the new reference method. This is because the new method based on gas chromatography is inherently different from the previous reference method based on infrared quantification. More importantly, the new reference method is not ideally suited for offshore use for several reasons, e.g. it is complex to operate and uses pressurised and flammable gases.

TUV NEL launched the OIWAM JIP in 2004 with following objectives:

- To identify the best practical means to implement the new reference method
- To establish best practice guidelines for oil in produced water sample taking and handling
- To develop a realistic set of acceptance criteria for the use of alternative oil-in-water analysis methods offshore
- To advise on how to relate results from the new reference method to those of the old method

A total of 10 organisations including BERR, the State Supervision of Mines (The Netherlands), BG Group, BHP Billiton, CNR International, Chevron, Kerr-McGee (now Maersk Oil North Sea UK), Marathon Oil, Shell UK, and Talisman Energy supported the project. The project was completed in 2005 with the final report [16] issued in July 2005.

Following on the OIWAM JIP, two major documents were produced, both of which were primarily based on the OIWAM JIP report. One was the publication of the OSPAR Guidance entitled "Oil in Produced Water Analysis – Guideline on Criteria for Alternative Method Acceptance and General Guidelines on Sample Taking and Handling" [17] in year 2006. The other one was a UK Government Guidance Note entitled "The Sampling and Analysis of Produced Water and Other Hydrocarbon Discharges" [12], which was published in September 2006.

Both of these documents have since played an important role in the implementation of the new reference method across the North Sea countries since 1st January 2007.

3.2 Produced Water Volume Determination (ProVol)

Knowing that there would be a new requirement of ±10% for the uncertainty in produced water volume determination and a possible accompanying requirement for annual verification, and the possibility that there would be an UK wide produced water trading scheme, it was clear that measurement of produced water discharge volume was to become an increasingly important issue.

Unlike the measurement of oil in produced water, there was no specified or generally agreed method for produced water volume determination. Neither was there a mechanism by which the accuracy of the reported data can be verified. In addition a brief survey carried out by TUV NEL early in 2004 indicated that methods used for produced water volume determination varied significantly from operator to operator,

and installation to installation. It also became obvious that there would be large differences in terms of accuracy of the different methods used.

Produced Water Volume Determination (ProVol) was therefore initiated in 2005 by TUV NEL. The project had the following objectives:

- To conduct a survey to find out methods currently used in calculating the volume of produced water discharged into the sea
- To carry out case studies to estimate uncertainties associated with some of these methods identified
- To develop best practice guidance in achieving the required ±10% uncertainty
- To identify verification methods and to develop verification procedures
- To carry out field verification

The project was sponsored by BERR, CNR International, Marathon Oil, Maersk Oil North Sea UK, Shell UK and Talisman Energy. It was completed with a final report issued to the sponsors in June 2007. The main outputs from the project are summarised below.

3.2.1 Survey of Current Produced Water Measurement Methods

Since there is currently no recommended standard method of produced water discharge measurement, the first aim of ProVol was to survey operators to find out which methods were currently being used in the North Sea. The survey found that the most common method, accounting for nearly half of the operators, was to install a meter on the discharge line. Meters commonly used for this purpose included electromagnetic, ultrasonic, Coriolis and orifice plates. Another relatively popular method of measuring the produced water flow was to infer it from the performance curve of a hydrocyclone, which is commonly used for the separation of oil and produced water. Some operators used well test data as the primary method of produced water volume measurement while others used it to complement one of the more popular methods.

3.2.2 Compliance with the Uncertainty Performance Target

The next part of ProVol was to conduct a series of case studies, using data supplied by the participating operators, to evaluate the uncertainty of each typical measurement method and relate it to the ±10% uncertainty standard. Ways of reducing the overall uncertainty of each method were also suggested. The uncertainty of direct metering depends heavily on factors such as installation effects and the frequency and uncertainty of calibration or verification. By following good metering practice and by conducting regular calibrations or verifications this method will comply with the performance target and is recommended as the primary method of produced water volume measurement. The case studies undertaken in this project revealed that to comply with the uncertainty performance targets it is necessary to undertake regular maintenance to minimise the uncertainty in the other measurement methods. In the hydrocyclone method the major uncertainty source is the build up of fouling of the equipment caused by the passage of produced water. With regular cleaning to reduce this build up, this method can comply with the performance target. The use of well

test data can comply if the meters measuring the flow of oil and water from the test separator are both calibrated regularly and to an uncertainty of less than 5%.

3.2.3 The Requirement for Verification

The final outputs from ProVol were two best practice guides which were made available to sponsors. The first described best practice in using the methods of produced water measurement outlined previously. This includes ways of minimising uncertainty so that they comply with the ±10% overall uncertainty performance target. It is important to note that the uncertainty of all of the measurement methods will change with time (for example through instrument drift or fouling build-up). To ensure continued compliance with the uncertainty performance target it is necessary to conduct regular verification tests. ProVol has produced a best practice guide in conducting these tests. This guide was supported by a series of field trials conducted on sponsor installations and includes recommendations of suitable methods of verification, including the use of clamp-on ultrasonic meters and tracer injection techniques.

PART B: VOLUME CORRECTION FACTORS FOR PRODUCED WATER

4 VOLUME CORRECTION

The UK OPPC Regulations (2004) stated that the produced water discharge volume should be reported at standard conditions of temperature and pressure (15 °C and 1.01325 bar (a)). However, the current (2005) statement of these Regulations does not refer to standard conditions. The equivalent Regulations in USA (EPA Region 6 NPDES Permit System) also require produced water discharge volume to be reported but do not specify standard conditions.

A 1 m^3 volume of produced water measured at 80°C, a temperature commonly experienced in practice, will reduce by approximately 2.5% when cooled to 15°C. In the context of the OPPC target of ±10% uncertainty in measured produced water volume, this may be a significant factor in determining whether an operator complies or otherwise. To account for this effect it is recommended that the measured volume should be referred to standard conditions. To apply this volume adjustment, it is therefore necessary to be able to formulate an equation to accurately evaluate the density of produced water over a comprehensive range of temperatures.

4.1 Pure Water Volume Correction

The thermal expansion factor for water is defined as the ratio of the density at the measured condition to the density at standard conditions. Several different formulations expressing the density of water as a function of temperature and pressure can be found in the literature. Most however are only valid for temperatures up to 40°C and when reproduced many do not make this limitation clear. This gives rise to errors when extrapolating to higher values. The International Association for the Properties of Water and Steam (IAPWS) currently provides the most reliable formulation for water density in the form of equations of state for pure water. The best

of these is the IAPWS-95 formulation [19], which allows the calculation of water properties over a very wide range of temperatures and pressures, and includes density, compressibility, viscosity, speed of sound and other thermodynamic properties. Unfortunately the formulation is complex. However Jim Watson prepared a series of simplified curve fits to this formulation for use within TUV NEL and these give manageable equations for everyday use. The density formula produced is valid over a temperature range of 0°C to 95°C and agrees with the full formulation to within 0.001 kg/m^3. This formula, giving the density of air-free water in kg/m^3 at 1.01325 bar, is shown in equation (1)

$$\rho_{IAPWS} = c_0 \cdot \left(\frac{1 + c_1 t_n + c_2 t_n^2 + c_3 t_n^3}{1 + c_4 t_n + c_5 t_n} \right) \qquad (1)$$

where t is the temperature (°C), t_n is the normalised temperature = t/100. The constants c_0 to c_5 are given by

c_0 = 999.84382 c_3 = -0.0309777
c_1 = 1.4639386 c_4 = 1.4572099
c_2 = -0.015505 c_5 = 0.0648931.

4.2 Application to Produced Water

In contrast to pure water, produced water is a complex mixture of different salts and other chemicals. Typically, and in terms of the behaviour for expansion, produced water can be represented as having similar salt composition to sea water however the salinity levels can be very much higher. Salinities up to 140 g/kg are commonly experienced while sea water has a typical salinity of up to 35 g/kg. It is not possible to assume that salt water has the same thermal expansion factors as pure water.

Two formulations which provide density of saline water were identified. The first of these is a set of state equations for salt water, including density, compressibility and speed of sound in a technical standard from UNESCO for use in Oceanography [20-21], in which formulations are included which are valid up to temperatures of 40°C and salinities of 40g/kg. It is noted that this formulation produces significant errors when extrapolated to high temperatures. This in most part is due to the use of a pure water formulation limited to 40 °C. A modified UNESCO formulation was produced based on the IAPWS formulation and this was used as the basis for formulation development. The second formulation was published by Isdale and Morris [22-23] as part of NEL research into desalination processes and published in 1972. This formulation covers temperatures ranging from 5°C to 95°C and salinities of up to 140 g/kg. Extrapolation to temperatures below 5°C and salinities below 35 g/kg using this formulation is not recommended.

Since both formulations provide good source data within their relative range and have some degree of acceptable extrapolation it was considered possible to combine these two equations to give a formulation that may be applied across the range of conditions suitable for produced water. A data table combining values from both formulations was derived. Data from any one formulation was discarded where differences

exceeded 0.05% and the value was in the extrapolated region of one of the formulations. This process provided a data set covering all of the proposed range of salinities and temperatures. A surface fit was then carried out on the derived data set. The proposed equation for the density of salt or sea water is given by:

$$\rho_{saltwater} = \left(\frac{a + b \cdot t + c \cdot t^2 + d \cdot t^3 + e \cdot S}{1 + f \cdot t + g \cdot t^2 + h \cdot S} \right) \quad \text{kg/m}^3 \qquad (2)$$

t = temperature (°C), S = Salinity (g/kg) and :

$a = 1000.625267$ $\quad d = 1.31139\times10^{-5}$ $\quad g = -1.75832\times10^{-5}$
$b = 2.340698$ $\quad e = 0.611416$ $\quad h = -1.73344\times10^{-4}$
$c = -2.31026\times10^{-2}$ $\quad f = 2.36919\times10^{-3}$

When compared with the actual values in the table, this formulation agreed to within 0.03% for temperatures down to 5°C. Where the temperature is below 5 °C and the salinity is below 50 g/kg the agreement is not so good with the residuals rising to 0.07 %. This region corresponds to temperatures below the maximum density of water and shows the selected function is not adequately following this turning point. The level of agreement between the data and the surface fit gives sufficient confidence to propose an equation for the density of saline water across the temperature range 0 °C to 95 °C and salinities up to 140 g/kg.

No uncertainty was given within the UNESCO publication. Isdale and Morris suggest that density was measured with an uncertainty of 0.02 % at high salinities and temperatures, and an uncertainty of 0.01 % at low concentrations rising to 0.1 % at higher temperatures and concentrations (60 °C - 130 g/kg) depending on the data source. The densities predicted by the combined formulation were compared with the original NEL experimental data and are shown in Table 1.

Table 2: Comparison of NEL experimental data to the formulation

Temperature C	Salinity g/kg	Density Measured kg/m3	Density Calculated kg/m3	Difference %
20.00	10.0	1.0058	1.0056	0.021
20.00	70.0	1.0512	1.0514	-0.022
20.00	130.0	1.0982	1.0982	-0.002
20.00	10.0	0.9992	0.9994	-0.019
20.00	70.0	1.0438	1.0440	-0.022
20.00	130.0	1.0896	1.0896	0.003
20.00	10.0	0.9902	0.9905	-0.027
20.00	70.0	1.0345	1.0345	-0.002
20.00	130.0	1.0795	1.0794	0.006
20.00	63.1	1.0179	1.0181	-0.018
20.00	63.1	1.0056	1.0056	-0.002
20.00	92.7	1.0454	1.0458	-0.034

20.00	92.7	1.0332	1.0335	-0.031
20.00	121.0	1.0618	1.0620	-0.016
20.00	148.5	1.083	1.0834	-0.033

Given the agreement found between the two formulations, it can be assumed that the proposed equation can be used with an uncertainty within 0.1 % below 5 °C and 50 g/kg and 0.05 % across the remaining range.

Beecroft [18] presented measured densities for produced water across a reasonably wide temperature range. At the time it was not required to measure the salinity of the water. This data is reproduced in Fig 1. This shows the density measured from the different samples vary by around ± 0.1 %. If the salinity is assumed to be 131.5 g/kg the above equation can be overlaid on this data and shown to reproduce the correct functional form and curve shape. As the salinity value has been assumed no inference can be made on the absolute agreement.

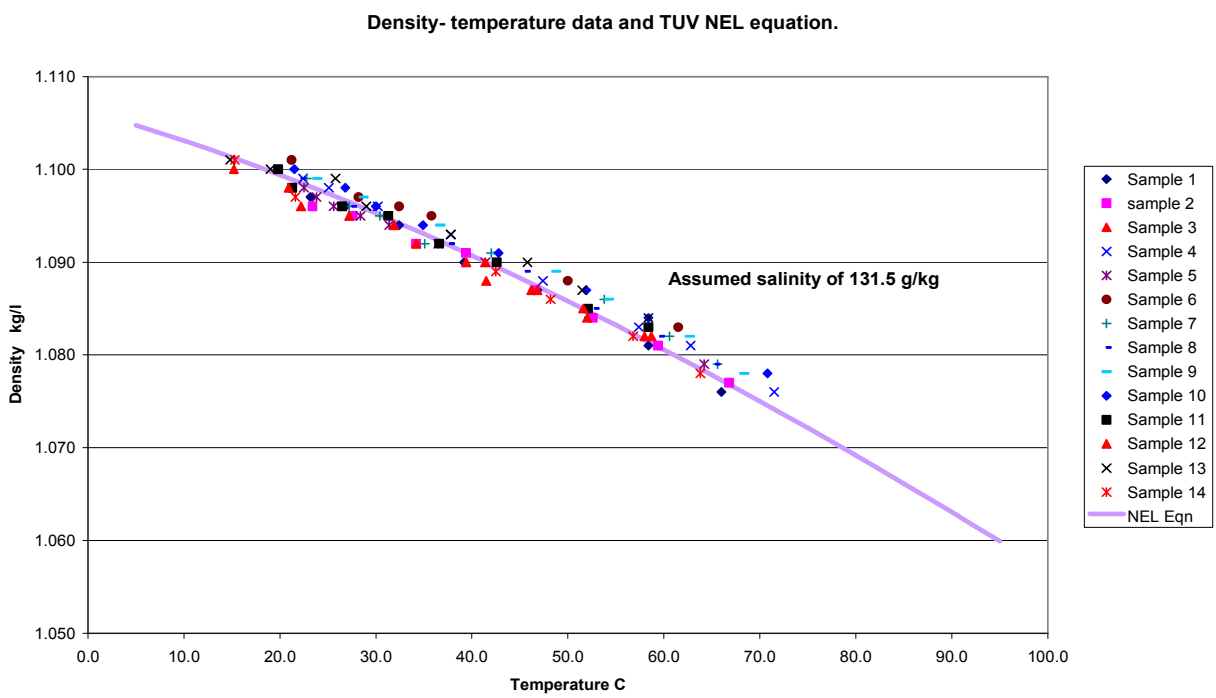

Fig 1: Comparison of produced water data and formulation.

4.3 Volume Correction Factor (Ctl)

Having derived a function for density, the volume correction factor (Ctl) can now be derived for the full range of conditions for which the density function is defined. The correction factor is calculated by evaluating the ratio of the density at measured and standard conditions. A reference temperature of 15 °C was chosen and Ctl values were calculated across the temperature range from 5 °C to 95 °C and salinities from 0 g/kg to 140 g/kg. The curves fitted to resultant data were restricted to relatively simple forms to provide a solution which could be easily applied in flow computers. This exercise showed that thermal expansion has a relatively weak dependence on

salinity and as such it was decided to provide a curve dependant on temperature only. The function below is the thermal expansion correction factor to adjust volumes to that at 15 °C.

$$ctl = a + b \cdot t^{1.5} + c \cdot \frac{1}{t^2} \tag{3}$$

Where t is temperature (°C)

a = 1.00246 b = -4.29 x10^{-5} c = 7.7713 x10^{-3}

Selecting a nominal volume and correcting it to standard conditions across the temperature and salinity range shows that this formula will provide correction to the volume (to 15 °C) agreeing with that derived from equation (2) to within ±0.2%. It is noted however that the differences are biased with respect to salinity within this ±0.2 % range.

4.4 Compressibility

The compressibility of salt water can be considered as being insignificant for most applications where produced water is discharged. The correction will amount to less than 0.02 % on volume when the pressure is 5 bar. Potentially in some applications, produced water may be measured in the high-pressure re-injection lines. This would require a volume correction of around 0.5 % at 100 bar pressure. A fit to data generated from the IAPWS-95 formulation provides an equation for the isothermal compressibility *Beta (B)* of pure water as given in equation (4):-

$$Beta = A_0 \cdot \left[\frac{(1 + A_1 t_n + A_2 t_n^{\ 2} + A_3 t_n^{\ 3})}{1 + A_4 t_n} \right] \tag{4}$$

where

t_n = normalised temperature = t/100
t is temperature (°C)
A_0=5.08821x10^{-10}
A_1=1.2639418
A_2=0.2660269
A_3=0.3734838
A_4=2.0205242

The compressibility is used to calculate the pressure correction factor (Cpl) and is given by:

$$Cpl = \frac{1}{1 - Beta \times P} \tag{5}$$

where P = pressure (barg)

A compressibility function is provided within the UNESCO equation of state. When compared with the pure water formula it is evident that the salinity has an effect on the compressibility which should not be discounted. The UNESCO equation was examined in more detail and again it shows a departure from the expected

compressibility when extrapolated above 40 °C and 35 g/kg. In assessing this effect, the potential error in compressibility is not expected to be significant in terms of produced water measurement; being estimated as being within 0.005 % on resultant volume. The UNESCO formulation is however complex and does not lend itself to a simple calculation procedure. A simplified formula was generated from the extrapolated UNESCO formula and including data for pure water from the IAPWS-95 formula. This gives the isothermal compressibility, *Beta (B)* as:

$$B_{Saltwater} = \left(a + b \cdot t + c \cdot S + d \cdot t^2 + e \cdot S^2 + f \cdot t \cdot S\right) \times 10^{-10} \quad \mathrm{Pa}^{-1} \qquad (6)$$

Where t = temperature (°C) , S = salinity (g/kg) and

$a = 5.0348$	$d = 2.513\times10^{-4}$
$b = -2.561\times10^{-2}$	$e = 1.593\times10^{-5}$
$c = -1.214\times10^{-2}$	$f = 8.368\times10^{-5}$

This formula is expected to provide an estimate of the compressibility to within 0.5 % except at the highest temperatures and salinity where the uncertainty is estimated to rise to 1 %. This will result in an uncertainty of 0.0001 and 0.0005 % in the resultant corrected volume.

4.5 Summary

The formulae presented have been developed by using data generated from other formulations rather than from raw experimental data. They provide a sound set of equations which may be used in practice when reporting the volume of saline produced water.

Clearly it would be advantageous to confirm these equations with sound laboratory based experimental data covering the density and compressibility functions. It should be stressed that experimental work should be carried out within an overall plan and in a controlled and thorough manner. Salinity, salt constituents and conductivity should be recorded when testing produced water and the results compared with the results from standard sea water constituents. It should also include examples of produced water compositions in addition to simulated sea water.

When taking samples of produced water for analyses, extreme care should be taken to ensure some of the salts do not precipitate out when the sample is cooled. Sodium chloride has a flat precipitation curve in relation to temperature and so little of this will precipitate. Other salts, although present in smaller quantities, will precipitate out hence changing the composition of the sample and also potentially damaging apparatus by precipitating out on the walls of containers valves and densitometer tubes.

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