Mass balance study of the Nedmag caverns

Modelling of magnesium salt dissolution and calculated squeeze volumes

NEDMAG

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---SUMMARY--

Upon request of Nedmag a second opinion study was carried out by NGConsulting on the report of the Mass balance study of the Nedmag caverns, revision 1. The main conclusion of NGConsulting was that the applied mass balance equations are correctly applied but that direct formation of bischofitic brine is a much more dominant dissolution mechanism than assumed by Nedmag. In addition it was advised to apply a temperature correction for the brine densities used.

The mass balance calculations were repeated following the recommendations of NGConsulting showing that due to volumetric expansion effects of direct dissolution of bischofite and thermal expansion of the underground magnesium chloride brine the new calculated squeeze volume is 5,201,954 m^3 which is 87 % of the BDS calculated volume of 5,994,612 m^3 (status 30-6-2015). The 5,201,954 m^3 squeeze volume with an accuracy of 5 % is in good agreement with a volume of 5,095,420 m^3 expected on basis of the TNO inversion study of the Nedmag subsidence bowl with an estimated accuracy of 6 %.

The mass balance calculated underground brine volume of 7,998,694 m^3 is 37 % higher than the calculated BDS volume of 5,821,174 m^3. Possible consequences of this higher volume for the conclusions of the Abandonment study of the Nedmag caverns will be investigated separately.

The new developed mass balance model for the calculation of squeeze volume and the resulting underground brine volume will be implemented by Nedmag in their cavern management system.

1. INTRODUCTION

On 26 March 2013 NEDMAG Industries Mining & Manufacturing B.V. in Veendam (Nedmag) has requested the Minister of Economic Affairs for approval of a modified production plan for potassium and magnesium salts. The plan announces a study into best practices to abandon the caverns after final production stop [1)].

On 3 October 2014 the Minister of Economic Affairs has approved the modified plan under certain conditions, among others Article 6, stating that Nedmag will investigate the discrepancy between the squeeze volume calculated with the BDS mass balance and the volume derived from inversion of the soil subsidence and the influence on soil subsidence predictions.

After pre-feasibility study and discussions with magnesium salt solution mining expert Norbert Grüschow from NGConsulting a study proposal was presented to State Supervision of Mines and TNO-Utrecht on 25 March 2015. The proposal was to do a history match of the Nedmag brine field from 1972 with the aim to improve the accuracy of the calculated squeeze volume. The study includes the following:

- A mass balance model will be developed and expanded with the salt lithology for future quantification of the amount of inert material in relation to bulking effects.
- The existing BDS model will be scrutinized with respect to used leaching phases and other assumptions.
- The effect of direct versus indirect dissolution of bischofite will be studied.
- The effects of connectivity of caverns will be incorporated.

On 30 October 2015 a report on the Mass balance study of the Nedmag caverns was issued [2)] and sent to SodM on 2 November 2015. On 26 November 2015 Nedmag requested NGConsulting to do a second opinion study on the Mass balance report. After numerous in-depth discussions a memo on the second opinion was issued by NGConsulting on 15 February 2017 [3)].

<u>NGConsulting second opinion</u>
The major conclusions of NGConsulting were that:

- direct dissolution of bischofite is also the main dissolution mechanism in connected Nedmag caverns, which has an impact on the volumetric calculations for the cluster, and
- a temperature correction has to be applied to the laboratory measured brine densities.

This report is an update of the 30 October 2015 report incorporating the aforementioned conclusions of NGConsulting, followed by conclusions regarding the accuracy of calculated squeeze volumes in relation to measured soil subsidence.

2. THE NEDMAG SOLUTION MINING PROCESS AND ITS MODELLING

2.1 The Nedmag solution mining process

Nedmag produces magnesium brine by solution mining of magnesium at a depth of 1300 to 1800 m in the Zechstein III formation. The first four caverns VE-1 to 4 have been developed from the first Well Head Centre 1 (WHC-1), caverns TR-1 to 9 were developed from WHC-2. Process water or dilute brine is injected as solvent into the bischofite/carnallite containing ZE-III 1b layer. In the early years also salt was produced from the carnallite containing ZE-III 2b/3b layers.

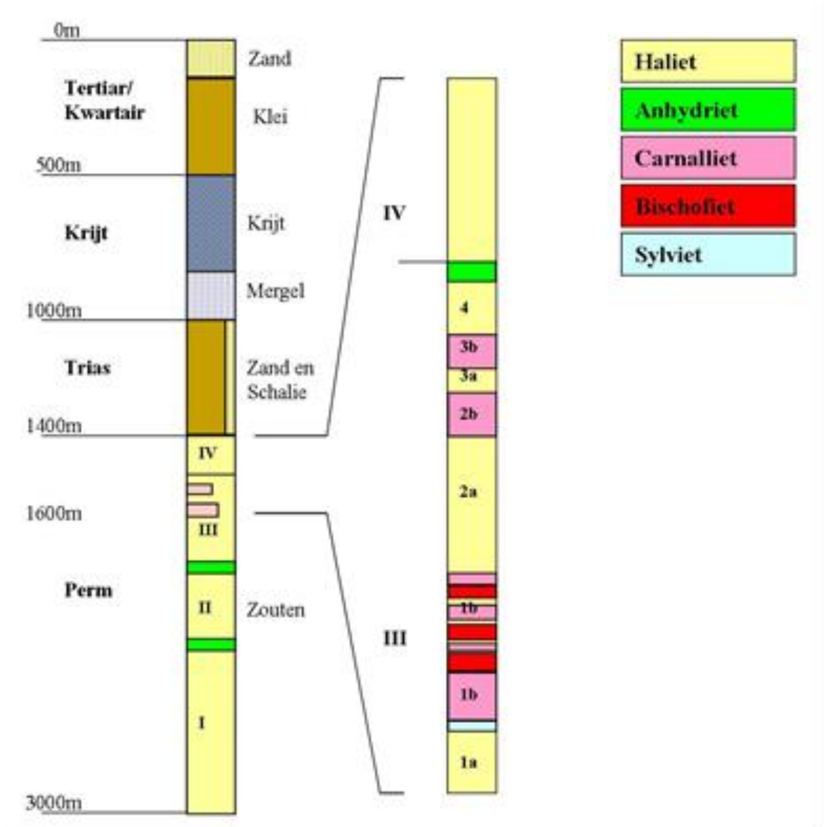
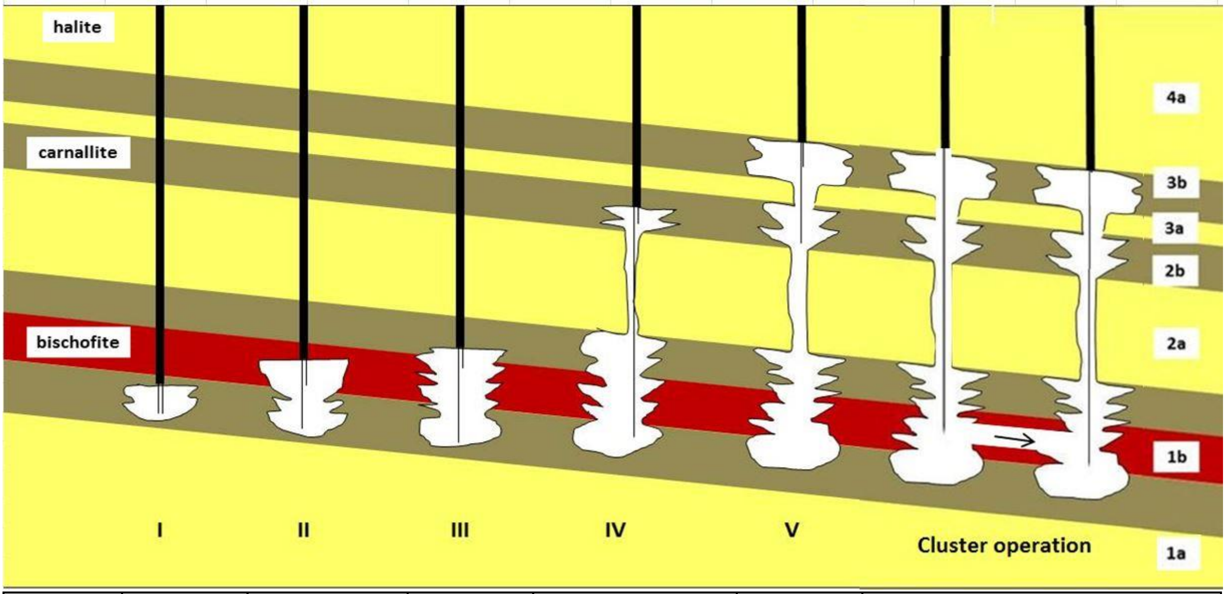


Figure 1: Typical salt lithology of a Nedmag cavern

In the development of the caverns the following 6 leaching phases can be distinguished:



Leaching mode	Direct	Direct	Direct	Indirect	Direct	Direct
Salt dissolved	Carnallite	Bischofite	Bischofite	2b/3b Carnallite/ 1b Bischofite	Carnallite	Bischofite

Figure 2: The six leaching phases of Nedmag caverns

In leaching phase 1 water or dilute brine is directly injected into the ZE-III 1b carnallite layer underlying the bischofite salt. In this phase a sump is prepared and a carnallitic (KCl-rich) brine is produced while sylvite precipitates. Uncontrolled upward leaching of overlying bischofite is prevented by an oil blanket.

The leaching path can be represented below by line OPC in the thermodynamic phase diagram (Figure 3). From O to P carnallite dissolves congruently until the maximum KCl solubility is reached at point P, thereafter from points P to C more carnallite dissolves while sylvite precipitates. At a temperature of 70 ^{o}C a saturated carnallitic brine is obtained containing 28 % $MgCl_2$ and 5 % KCl.

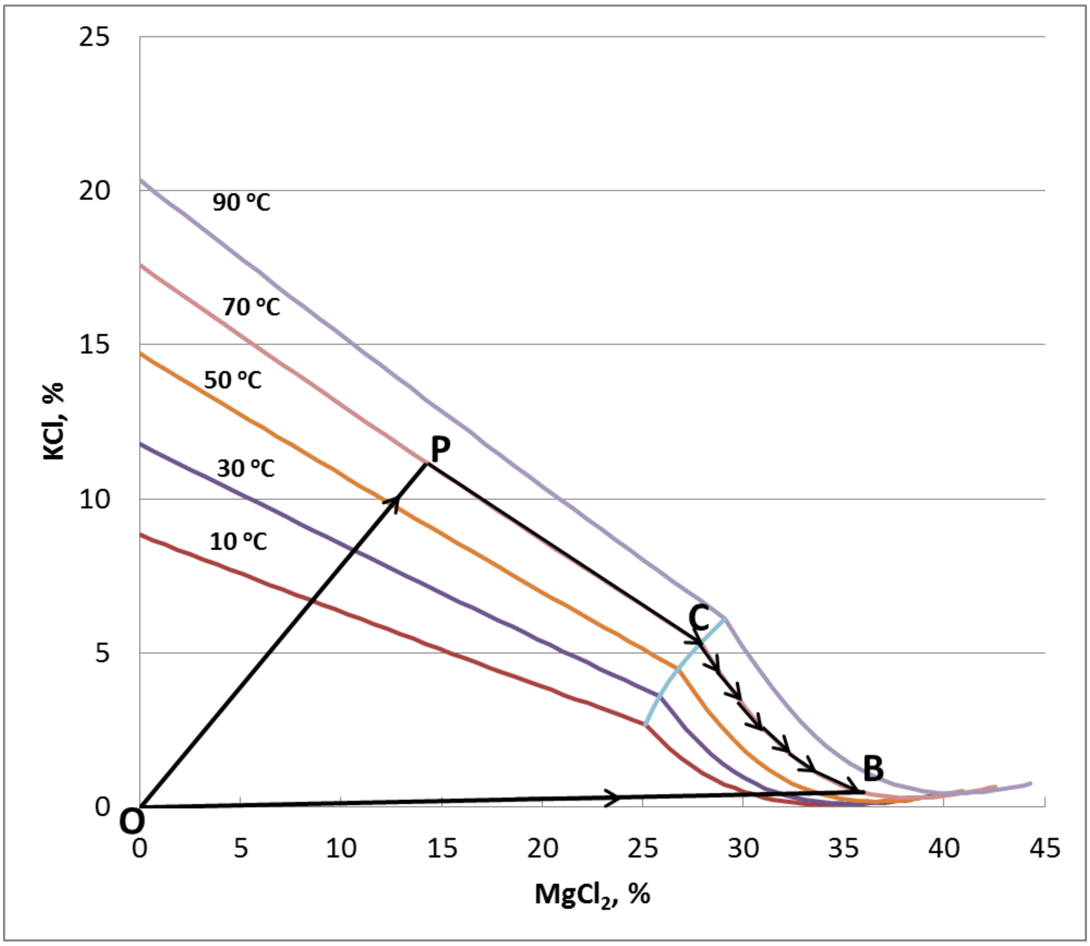


Figure 3: The $MgCl_2$/KCl phase diagram

After the desired sump volume is obtained the oil blanket and/or the injection level are raised into the bischofite containing ZE-III 1b section and bischofite selectively dissolves in leaching phase 2 according to leaching path OB (direct dissolution) in Figure 3. At point B a saturated bischofitic brine is formed containing 36 % $MgCl_2$ and 0.5 % KCl. In order to meet the KCl saturation a small amount of carnallite or sylvite dissolves. In addition small amounts of halite and kieserite will dissolve parallel to the bischofite.

After further upward displacement of the oil blanket and/or injection point in leaching phase 3 the solvent is injected in the top of the ZE-III 1b section.

In the original leaching phase 3 dissolution concept [2)] solvent first contacts carnallite forming a carnallitic brine according to leaching path OPC. The carnallitic brine volume not fitting into the formed cavern space overflows to the lower bischofite containing section. This internal overflow volume is reduced by any downfall of destabilised inert material and precipitates. The resulting overflow dissolves bischofite and a bischofitic brine is formed according to leaching path CB while KCl precipitates in the form of secondary carnallite.

According to the present insights from NGConsulting [3] and Nedmag supported by computational fluid dynamics simulations [4], because of the strong local turbulence, solvent and saturated bischofitic cavern brine in the ZE-III 1b cavern are so well mixed that the cavern $MgCl_2$ concentration does not fall below 28 %. As a result selective bischofite dissolution takes place and the direct dissolution path OB is followed. Another consequence is that any downfall of insoluble inert material is irrelevant for the volumetric balance in the cavern.
This new concept of direct formation of bischofite for leaching phase 3, in this report named as leaching phase 3DL, with injection high-up in ZE-III 1b layer results in the direct dissolution of bischofite identical to leaching phase 2.

In leaching phase 4 the injection point and oil blanket are raised to the lower ZE-III 2b carnallite section, where there is no bischofite present, while the production point remains in the lower ZE-III 1b section. Solvent injected in ZE-III 2b forms a carnallitic brine that overflows through the borehole to ZE-III 1b section where it contacts bischofite and forms a bischofitic brine. This situation with physically separated injection in ZE-III 2b and production from ZE-III 1b is the only one in which the indirect leaching path OPCB is followed.

In leaching phase 5 the injection point and oil blanket are raised to the upper ZE-III 3b carnallite layer and the production point is raised to the lower ZE-III 2b carnallite layer. In this phase carnallitic brine is produced according to leaching path OPC as for leaching phase 1.

Until the year 1993 the caverns were operated close to litho-static pressures with a “room and pillar” solution mining approach. After successful demonstration of the squeeze concept between 1993 and 1995 the TR wells, except TR-9, are producing at 60 – 80 bar sub-lithostatic conditions.

Soon after start-up in October 1982 a pressure connection was found to be between TR-1 and TR-2. In the period from November 1996 onwards more TR caverns gradually interconnected into one large cluster. In September 2009 VE-4 also connected to the TR cluster. During the last VE-3 workover in November 2006 a connection with VE-2 was noticed.

Currently the Nedmag caverns consist of two clusters and two separate caverns:

- The TR cluster consisting of TR-1/2/3/4/5/6/7/8 & VE-4.
- The VE cluster consisting of VE-2 & VE-3.
- VE-1 developed in the ZE-III 2b/3b section only.
- TR-9 in development since May 2012 in the ZE-III 1b section only.

In the cluster operation which is currently applied to the TR cluster, solvent is typically injected into the shallower ZE-III 1b sections. Due to the turbulent mixing of solvent and cavern brine, selective direct bischofite dissolution following leaching path OB is also applicable to ZE-III 1b injection caverns. Whereas in version 1 of the report on the Mass balance study of the Nedmag caverns indirect formation of bischofitic brine was assumed [2).].

2.2 Nedmag mass balance models

2.2.1 The BDS model

The Brine Data System (BDS) model was developed in 1995 and is in use to monitor the development of the various volumes due to the Nedmag solution mining process since 1972. It is primarily based on a mass balance with inputs of measured injection and production brine volumes and concentrations per cavern. At a given leaching phase BDS calculates the quantities of dissolved salt, precipitates, as well as the squeeze volume and the total underground brine volume. The squeeze volume is defined as the measured volume of brine coming to surface in excess to what could be expected from the injection fluid without cavern convergence.

One characteristic BDS feature is that it assumes that brine composition can be represented by a mixture of the following three components: saturated bischofitic brine, saturated carnallitic brine and water. In addition it is assumed that the caverns are filled by a two phase system of saturated carnallitic brine floating on top of a saturated bischofitic brine with compositions independent on depth. In case of the production of under-saturated brine it is assumed that part of the injection water shortcuts directly to the brine production flow.

The BDS calculations are set-up for a single cavern operation. The interconnection of caverns creates a mismatch between injection fluid and brine production per cavern. Therefor meaningful squeeze and underground brine volumes can only be obtained by summating the values of the individual caverns.

The accuracy of the BDS model calculations for the total underground brine volume has been estimated by Renier [5)]. His main findings were that the selected leaching phases were not always correct and that the choice for indirect or direct formation of bischofitic brine has a significant effect on the volumes calculated. Renier recommended to study the following:

- The effect of depth (temperature) on saturated brine compositions and densities. A variation analysis for the total height difference between the caverns showed that this introduces an inaccuracy of 4 % of the calculated squeeze volume. This result has been reported by Nedmag in 2012 [6)].

- The effect of pressure, depth and shape on cavern convergence. This is part of the Nedmag Abandonment study [7)].
- The effect of brine exchange between interconnected caverns, which is part of this study.

2.2.2 The mass balance model

Since BDS model relies on the physically incorrect assumption that all brine compositions can be split into: saturated carnallitic and bischofitic brine and water a standard more exact mass balance model was prepared. In this model it is assumed that the undiluted produced brine composition is representative for the entire cavern content. This avoids the use of a standard bischofitic brine composition. However the use of standard saturated carnallitic brine remains necessary in the case of indirect dissolution in leaching phase 4. The used model equations have been described previously [8)] and are, including a small textual correction by NGConsulting [3)], given in Appendix I.

3. MODEL CALCULATIONS

3.1 General

On basis of the operational data for the period of 1972 till June 2015 mass balance calculations were carried out with the new mass balance model. A monthly mass balance was made up for each individual cavern. By summating the corresponding volume effects over all caverns, the resulting squeeze volume and underground brine volume for the whole Nedmag brine field were obtained.

Section 3.2 describes the mass balance calculations with the original or injection depth revised leaching paths. The latter with and without density correction for cavern temperature. In these calculations the original assumptions of indirect formation of bischofitic brine for leaching phase 3 were maintained.

Section 3.3 describes the mass balance calculations with the new direct formation of bischofitic brine according to leaching phase 3DL, with and without density correction for cavern temperature.

In section 3.4 an analysis was made how to model the leaching process in the cluster operation of caverns connected through the ZE-III 1b layer.

3.2 Mass balance model calculations: original leaching phases, revised leaching phases and temperature correction

In the case: MB original all leaching phases 1 till 5 and brine densities, defined at 20 ^{o}C, were kept identical to the ones used in the BDS calculations.

The designation of leaching phases in the BDS calculations was checked against the actual injection depth as reported in historical monthly reports in relation to the salt lithology per cavern. It was found that there were a number of months in which was injected into the ZE-III 1b bischofite (leaching phase 2) instead of the overlying ZE-III 1b carnallite (leaching phase 3). This gives more direct production of bischofitic brine than accounted for in the original BDS calculations.
In the case: MB revised LF's the corrected leaching phases 1 till 5 were applied but maintaining the original leaching path assumptions and brine densities.

The case: revised LF's with T-correction is a repeat of the revised LF's calculation but now with brine densities of the produced brine as well as the cavern brines corrected for cavern temperatures of 67 ^{o}C for ZE-III 1b caverns or 63 ^{o}C for ZE-III 2b/3b caverns. The original leaching path assumptions were maintained.

Case	Squeeze volume		Underground brine volume	
	m^3	% of BDS	m^3	% of BDS
BDS	5,994,612	100	5,821,784	100
MB original	6,983,311	116	5,280,514	91
MB revised LF's	6,208,914	104	6,484,981	111
MB revised LF's with T-correction	5,692,016	95	7,151,617	123

The new mass balance calculations with the same original input parameters gives 16 % more squeeze volume and 9 % less total underground brine volume than BDS. This difference is mainly due to the imperfections in the BDS model.

With revised leaching phases, incorporating a higher contribution of the more expansive direct formation of bischofitic brine, the squeeze volume reduces importantly but still is 4 % higher than the original BDS value at an 11 % higher total underground brine volume.

Although the brine density reduction due at a temperature increase from 20 to 67 ^{o}C of 2 – 3 % is relatively small, its effect on squeeze volume is as high as 9%. This is in general agreement with the findings of NGConsulting and is due to the fact that the total volumetric brine expansion is concentrated in a smaller partial volume [3)].

<u>Example TR-9</u>
The strong effect of a relative small density correction is best demonstrated by an example calculation based on the operational data of September 2014 for well TR-9. In this period 7,664 m^3 of diluted brine (@ 64.5 ^{o}C) was produced and 3,937 m^3 water was injected in leaching phase 2. Given the applied dilution volume of 954 m^3 the

undiluted cavern brine production was 6,710 m^3 (@ 67 ^oC). In steady state, depending on the diluted brine density used, the injection water forms 14,707 or 14,797 tons brine of cavern composition and dissolves 6,708 or 6,764 m^3 salt.

At a cavern brine density of 1.307 t/m^3 some 327 m^3 more brine was formed in 56 m^3 more dissolved volume, giving an additional 271 m^3 brine production without squeeze.

Brine produced				Undiluted brine formed		Dissolved	Undiluted Production	Actual undiluted	Squeeze
Diluted		Undiluted		from solvent		volume	without squeeze	production	volume
Temp, ^oC	t/m^3	Temp, ^oC	t/m^3	t	m^3	m^3	m^3	m^3	m^3
20.0	1.296	20.0	1.338	14,707	10,992	6,708	4,284	6,710	2,426
64.5	1.270	67.0	1.307	14,797	11,319	6,764	4,555	6,710	2,155
Diff				90	327	56	271		-271
Ratio	0.980		0.977	1.006	1.030	1.008	1.063		0.888

Since the squeeze volume is defined as the cavern production (6,710 m^3) minus the theoretical production without squeeze (4,555 m^3) the extra 271 m^3 brine expansion is directly reflected in the production volume without squeeze. Thereby the calculated squeeze volume is reduced from 2,426 m^3 by 271 m^3 to 2,155 m^3 giving a relative reduction of more than 11.2 % in this particular operational period for TR-9.

3.3 Mass balance model calculations: effect direct bischofite dissolution and temperature

Since according to NGConsulting [3)] and Nedmag current insights indirect formation of bischofitic brine is a mechanism valid only for leaching phase 4, the MB revised calculations were repeated for the following cases:

- Case: MB revised LF 3 --> 3 DL assuming direct leaching of bischofite in leaching phase 3, whilst maintaining the 20^oC densities.
- Case MB revised LF 3 --> 3 DL with T-correction, assuming direct leaching of bischofite in leaching phase 3 including brine densities corrected for a temperature of 67^oC for ZE-III 1b or 63 ^oC for ZE-III 2b/3b caverns for all leaching phases.

The results are given in the table below, in which for reasons of comparison also the original BDS volumes are included.

Case	Squeeze volume		Underground brine volume	
	m^3	% of BDS	m^3	% of BDS
BDS original	5,994,612	100	5,821,784	100
MB revised LF's	6,208,914	104	6,484,981	111
MB revised LF 3 --> 3DL	5,735,795	96	7,316,829	126
MB revised LF 3 --> 3DL and T-correction	5,201,954	87	7,998,694	137

It is clearly demonstrated that the squeeze volume is reduced by 473,119 m^3 by the volumetric expansion effect of direct formation of bischofitic brine and by an additional 533,841 m^3 through thermal expansion effects. By the combined expansion effects a final squeeze volume of 5,201,954 m^3 results which is 87 % of the original BDS value. As a side effect the total underground brine volume is increased by 37 % to 7,998,694 m^3.

3.4 Mass balance model and clustering

In the first version of the mass balance report [2)] it was explained that In the historical development of the Nedmag brine field more and more caverns became interconnected through the ZE-III 1b layer.

<table>
<tr><th>Well</th><th>VE-1</th><th>VE-2</th><th>VE-3</th><th>VE-4</th><th>TR-1</th><th>TR-2</th><th>TR-3</th><th>TR-4</th><th>TR-5</th><th>TR-6</th><th>TR-7</th><th>TR-8</th><th>TR-9</th></tr>
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<tr><td>sep-09</td><td></td><td colspan="2">Cluster 8</td><td colspan="9">Cluster 9</td><td></td></tr>
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Figure 4: Time development of connections between the Nedmag caverns

The connectivity of caverns is actively used by injecting in one cavern and producing brine from other caverns. The main dissolution mechanism for a cluster operation that was applied in version 1 of the Nedmag mass balance report was indirect formation of bischofitic brine [2)].

According to current knowledge [3,4)] the $MgCl_2$ concentration in a ZE-III 1b cavern does not fall below 28 % due to the presence of saturated bischofitic cavern brine and effective mixing of the solvent with the cavern brine. This means that there is no carnallite dissolution potential, hence direct formation of bischofitic brine is also the prevalent mechanism in an injection cavern.

In the original cluster treatment [2)] connected caverns were treated as one system with combined injection/production flows and mixed brine concentrations. However in this approach all distinction is lost between upper ZE-III 2b/3b and lower ZE-III 1b caverns. It was realised that for a more detailed description the number of clusters has to be increased importantly by discriminating periods of:

- Injection and production from the connected ZE-III 1b sections with direct dissolution of bischofite.
- Injection into ZE-III 2b/3b caverns and production from the connected ZE-III 1b section with indirect dissolution of bischofite.
- Injection and production from ZE-III 2b/3b caverns with partial bleed of carnallitic brine to the ZE-III 1b section.

- Production of ZE-III 1b brine through an upper ZE-III 2b/3b cavern as was experienced during the pilot squeeze test with TR-4 and TR-6 in 1993 till 1995.

Given the complex volumetric interactions and the fact that the status of the separate upper 2b/3b caverns is of prime importance for future abandonment it is found that mass balance calculations on basis of single caverns as was done in the case:
LF 3-->3DL with temperature correction is a better approach.

The effect of clustering at the ZE-III 1b section can then be incorporated by summation of the individual volumes of the connected caverns.

In the table below the volumes after clustering are given for the status June 2015.

Cavern/cluster	Squeeze volume, m^3	Underground brine volume, m^3		
	Total	ZE-III 1b	ZE-III 2b/3b	Total
VE-1	21,489	0	175,824	175,824
TR-9	21,657	346,481	0	346,481
VE 2/3	145,201	675,441	412,704	1,088,145
TR 1-8/VE-4	5,013,607	4,692,290	1,695,956	6,388,246
Totaal	5,201,954	5,714,211	2,284,483	7,998,695

Of the 7,998,95 m^3 total underground brine volume some 5,714,211 m^3 is present in the ZE-III 1b caverns and 2,284,483 m^3 in the upper ZE-III 2b/3b caverns. Please note that in situations of a cavern with an upper ZE-III 2b/3b and a lower ZE-III 1b cavern the total squeeze volume can be calculated but not its distribution. In such situations a default distribution, based on laboratory creep testing of carnallite and bischofite, of 5 % for an upper ZE-III 2b/3b cavern and 95 % from a lower ZE-III 1b cavern was assumed.

4. DISCUSSION

In 2011 an inversion study was carried out by TNO [9)] on the subsidence measurements for the period of 1993 till 2010. From this study a mismatch of about 15 % was found between the BDS calculated squeeze volume and the squeeze volume as determined by inversion of the subsidence bowl. According to TNO this discrepancy can be due to either an error in the geomechanical model or a positive structural error in the determination of the total squeeze volume from production data.

Under the assumption of a constant mismatch factor of 0.85 for the whole production period of 1972 till June 2015 an inversion volume of 5.095,420 m^3 is expected from the BDS calculated squeeze volume of 5,994,612 m^3.

Case	Squeeze volume		Underground brine volume
	m^3	% of Inv. volume	m^3
Inversion volume, 85 % of BDS	5,095,420	100	
MB revised LF 3 --> 3DL and T-correction	5,201,954	102	7,998,694

The detailed studies of Nedmag and NGConsulting show that the squeeze volume calculated with direct bischofite dissolution and temperature corrected densities is only 2 % higher than the expected inversion volume with its own inaccuracy. The squeeze volume agreement is very good taken in view a combined inaccuracy of 5 % for the volume measurements and chemical analysis of solvent and production brine and an estimated 6 % inaccuracy for the inversion volume (1 σ at 3.5 mm).

5. CONCLUSIONS

New mass balance calculations of Nedmag and NGConsulting incorporating the expansion effects of direct dissolution of bischofite in the ZE-III1b section and a temperature corrected brine density give a squeeze volume of 5,201,954 m^3 for the Nedmag brine field operation for the period of 1972 till June 2015. This squeeze volume is 87 % of the BDS calculated volume.

The new squeeze volume of 5,201,954 m^3 is in good agreement with the expected inversion volume of 5,095,420 m^3 based on the inversion study carried out by TNO in 2011. The 2 % relative difference can be fully explained by an inaccuracy of 5 % for the calculated squeeze volume and an expected inaccuracy of 6 % for the inversion volume.

Since the subsidence predictions in the 2013 Winningsplan are based on 85 % of the predicted BDS squeeze volumes there is no need to update the subsidence predictions herein. However the effects of an up to 37 % higher total underground brine volume on future abandonment have to be investigated.

The new developed mass balance model for the calculation of squeeze volume and the resulting underground brine volume will be implemented by Nedmag in their cavern management system.

REFERENCES

1. Winningsplan kalium- en magnesiumzoutwinning 2013, Nedmag Industries Mining & Manufacturing B.V., Winningsvergunning Veendam, 26 maart 2013.
2. Mass balance study of the Nedmag caverns, J. Visser, Veendam 30 October 2015.
3. Second opinion for Nedmag Cavern Mass balance. NGConsulting, Sondershausen, 15 February 2017.
4. W.R Velema, H. Bruining, J. Bullen en J. Visser. Natural Convection Effects on Magnesium Solution Mining. 12th European Conference on the Mathematics of Oil Recovery, Oxford UK, 6-9 September 2010.
5. Gedrag van Magnesiumzouten tijdens de Winning in de Concessie van Nedmag te Veendam en een daaruit volgende volumebepaling van het Complex van Cavernes van WHC-2. W. Renier, MSc Thesis TU Delft, 1 september 2006.
6. Het ondergronds pekelvolume en onzekerheidsanalyse hiervan bij de Nedmag zoutwinning. Interne Nedmag notitie, J. Visser, Veendam, 25 april 2012.
7. Abandonment study Nedmag caverns. Cavern squeeze modelling and geophysical analysis of brine permeation and containment. Well Engineering Partners B.V., dr.ir. A.J.H.M. Duquesnoy, Hoogeveen 31-3-2015.
8. Nauwkeurigheidsanalyse BDS modelberekeningen. Interne Nedmag Notitie, J. Visser, Veendam, januari 2013.
9. Nedmag Veendam inversie bodemdaling TNO-rapport (060-UT-2011-00687). P.A Fokker, Utrecht, 8 april 2011.

APPENDIX I

Leaching phase 1

The development of a cavern starts with the creation of an undercut in the lower section of the 1b carnallite salt. Dissolution of the overlying bischofite salt is prevented by installing an oil blanket. In phase 1 water or diluted brine (M_1) is injected and the salts: carnallite (C), halite (H) , kieserite (K) go into solution forming brine (M). Due to the incongruent dissolution behaviour of carnallite the sylvite ($S\downarrow$) precipitates simultaneously. Typically a carnallitic brine is formed typically with: 28 % $MgCl_2$, 5.2 % KCl, 2 % NaCl and 1.3 % $MgSO_4$ and a density of 1.33 t/m^3 @ 20^{o}C (ρ_{CB}) at saturation.

For leaching phase 1 the following mass balance equations are apply:

Total mass	$M_1 + C + H + K = M + S\downarrow$	(1)
Magnesium chloride	$m_1M_1 + m_cC = mM$	(2)
Potassium chloride	$s_1M_1 + s_cC= sM + S\downarrow$	(3)
Sodium chloride balance	$h_1M_1+ H = hM$	(4)
Kieserite balance	$k_1M_1 + k_kK = kM$	(5)

The symbols: m, s, h and k represent the dissolved mass concentrations of $MgCl_2$, KCl, NaCl and $MgSO_4$ in the injection fluid (subscript 1) or of the brine formed. The symbols m_c, s_c and k_k represent the $MgCl_2$ content in carnallite, the KCl content in carnallite and the $MgSO_4$ content in kieserite respectively.

Combination of eqn's (2), (3), (4) and (5) and substitution in eqn. (1) yields:

$$M = M_1 (1-m_1/m_c (1-s_c) - h_1 - k_1/k_k - s_1) / (1 - m/m_c (1-s_c) - h - k/k_k - s) \qquad (6)$$

Insertion of known mass of injected water or brine and measured concentrations of injection and product brine allows the calculation of the mass of brine (M) formed. Insertion of M in eqn's (2) till (5) quantifies the mass of the dissolved salts: C, H, K and precipitate $S\downarrow$.

The net volume of the carnallite cavity for lithostatic pressure conditions, i.e. in the absence of cavern convergence, is calculated using the respective salt densities through:

$$\Delta V_{C,cav} = C/\rho_C + H/\rho_H + K/\rho_K - S\downarrow/\rho_{Sy} \qquad (7)$$

Finally the volume of brine produced under litho-static conditions is calculated through:

$$\Delta V_{prod} = M / \rho_{CB} - \Delta V_{C,cav} \qquad (8)$$

	Carnallite	Bischofite	Kieserite	Halite	Sylvite
ρ, t/m3	1.60	1.60	2.57	2.14	1.99
$MgCl_{2,\,\%}$	34.28	46.86			
KCl, %	26.84				
NaCl, %					
$MgSO_{4,\,\%}$			86.98		

Leaching phase 2 with direct formation of bischofitic brine

After an undercut has been developed the oil blanket is withdrawn allowing contact of the injected water or brine with bischofite salt. As a result bischofite dissolves (B) from the 1b section and a bischofitic brine is produced typically containing: 36 % $MgCl_2$, 0.5 % KCl, 0.5 % NaCl and 0.45 % $MgSO_4$ and a density of 1.38 t/m3 @ 20 ^oC (ρ_{BB}) at saturation.

For this phase the following mass balance equations are valid:

Total mass	$M_1 + C + B + H + K = M$	(9)
Magnesium chloride	$m_1M_1 + m_cC + m_BB= mM$	(10)
Potassium chloride	$s_1M_1 + s_cC= sM$	(11)
Sodium chloride	$h_1M_1+ H = hM$	(12)
Kieserite	$k_1M_1 + k_kK = kM$	(13)

The symbols: m, s, h and k represent the mass concentrations of $MgCl_2$, KCl, NaCl and $MgSO_4$ in the injection fluid (subscript 1) or in the brine formed. The symbol m_B represent the $MgCl_2$ content of bischofite salt.

Combination of eqn's (10), (11), (12) and (13) and substitution in eqn. (9) yields:

$$M = M_1 (1- s_1/s_C*(1-m_C/m_B)- m_1/m_B – h_1 – k_1/k_k) / (1 – s/s_C*(1-m_C/m_B)- m/m_B – h – k/k_k) \quad (14)$$

Insertion of the known mass of injected water or brine and measured concentrations of injection and product brine allows the calculation of the mass of brine (M) formed. Insertion of M in eqn's (10) till (13) allows the calculation of mass of the dissolved salts: B, C, H, K.

The net volume of the cavity without for lithostatic pressure conditions without convergence, is calculated using the respective salt densities through:

$$\Delta V_{B,cav} = C/\rho_C + B/\rho_B + H/\rho_H + K/\rho_K \quad (15)$$

Finally the volume of brine produced under litho-static conditions is calculated through:

$$\Delta V_{prod} = M/\rho_{BB} - \Delta V_{B,cav} \quad (16)$$

Leaching phases 3 and 4 with indirect formation of bischofitic brine

After the bischofitic cavern had reached its optimum diameter the injection point was raised either into the 1b carnallite layer above the bischofite salt (phase 3) or the 2b/3b carnallite layer (phase 4). As a result the injected water or brine initially forms a carnallitic brine in a carnallite cavity. The carnallite dissolution process is identical to phase 1 described by eqn's: (1) to (7). The part of the carnallitic brine that doesn't fit into the carnallitic cavity overflows to the underlying 1b bischofite cavity according to:

$$\Delta V_{overflow} = M / \rho_{CB} - \Delta V_{C,cav} \qquad (17)$$

In the bischofite cavity the carnallitic brine ($M_1 = \Delta V_{overflow} * \rho_{CB}$) dissolves bischofite salt and a bischofitic brine is produced. As a result of the increased $MgCl_2$ concentration part of the carnallite (C↓), kieserite (K↓) and halite (H↓) precipitate. The effects of the carnallitic brine transformation can be described by:

Total mass balance:	$M_1 + B = M + C\downarrow + K\downarrow + H\downarrow$	(18)
Magnesium chloride balance:	$m_1M_1 + m_BB = mM + m_CC\downarrow$	(19)
Potassium chloride balance	$s_1M_1 = sM + s_C C\downarrow$	(20)
Sodium chloride balance	$h_1M_1 = hM + H\downarrow$	(21)
Kieserite balance	$k_1M_1 = kM + k_kK\downarrow$	(22)

After some manipulation of eqn's (19), (20), (21) and (22) followed by substitution in eqn. (18) gives:

$$M = M_1 (1- s_1/s_C*(1-m_C/m_B)- m_1/m_B - h_1 - k_1/k_k) / (1 - s/s_C*(1-m_C/m_B) - m/m_B - h - k/k_k) \qquad (23)$$

This equation is identical to equation (14).

Insertion of known mass of injected water or brine and measured concentrations of injection brine allows the calculation of the mass of the overflow $\Delta V_{overflow}$. The underlying assumption is that a saturated carnallitic brine. Inserting the overflow as M_1 allows the calculation of the bischofite brine formed (M). With eqn's (19) till (22) the mass of the dissolved B and precipitates: C↓, H↓, K↓ is calculated.

Leaching phase 5

The volume effects resulting from production of carnallitic brine though injection and production from the 2b/3b layer can be fully described are identical to the ones derived for leaching phase 1.

Calculation of squeeze volume

The net volume of the cavity without for litho-static pressure condition convergence for the 1b bischofite section is calculated using the respective salt densities through:

$$\Delta V_{B,\,cav} = B/\rho_B - C\downarrow/\rho_C - H\downarrow/\rho_H - K\downarrow/\rho_K$$

The volume of brine produced that would be produced under litho-static conditions is calculated through:

$$\Delta V_{prod} = M / \rho_{BB} - \Delta V_{B,cav}$$

The squeeze volume is defined as the excess of brine coming to surface over the calculated litho-static contribution:

$$\Delta V_{squeeze} = \Delta V_{surface} - \Delta V_{prod}$$

In case of a cluster of N caverns the volumetric effects of the constituting individual caverns are summated according to:

$$\Delta V_{cluster} = \sum_{1}^{N} \Delta V_{cavern}$$