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## Article

# The Need of Chloride-37 Enrichment for Molten Salt Fast Reactors

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**Abstract:** The use of natural chloride in the salt fuel has been sometimes promoted for the chlorine based molten salt fast reactor using for example NaCl-UCl<sub>4</sub>-UCl<sub>3</sub>. Most of the chemistry based R&D has been carried out on natural chloride, while in reactor physics most of the calculations are based on enriched chloride-37. In any case, the use of natural chloride (75.77% <sup>35</sup>Cl and 24.23% <sup>37</sup>Cl) induces specific ecological and neutron economical issues. An ecological issue is the production of <sup>36</sup>Cl by neutron activation of <sup>35</sup>Cl. Chlorine-36 is a soluble long live nuclide that makes it a 'first' nuclide in the safety assessment of the repository. We explore the build-up of <sup>36</sup>Cl with burnup for various <sup>37</sup>Cl (activation product) enrichment. The neutron economical aspect is gained by achieving reactor criticality with a lower amount of fissile material achieved through the use of enriched chloride-37. The criticality (*k*) of a core is much larger for enriched chloride than for the natural one. The reactor with 99% <sup>37</sup>Cl would have a *k*<sub>99</sub>/*k*<sub>nat</sub> of 1.04346 which would allow to reduce the required uranium enrichment and thus the fuel cost. This reactivity gain is evaluated for various <sup>37</sup>Cl enrichment factors to estimate uranium enrichment gain achievable through <sup>37</sup>Cl enrichment. However, from economical point of view it could be of interest to use as some kind of compromise solution natural NaCl, which will be analysed, too. Production/enrichment of <sup>37</sup>Cl can be performed by physical separation e.g. gas centrifugation of <sup>1</sup>H<sup>35/37</sup>Cl or by chemical separation using anion partitioning and elution of <sup>23</sup>Na<sup>35/37</sup>Cl on solid adsorbent columns or in liquid – liquid extraction systems. These techniques require however extensive investigations including chemical thermodynamics and hydrodynamics. Comparisons are suggested on the basis of the separation factor  $\alpha$ . Recommendations are finally given for utilising <sup>37</sup>Cl in the fast molten salt reactor. **The enrichment work for <sup>37</sup>Cl is smaller than the work needed for <sup>235</sup>U enrichment.**

**Keywords:** nuclear; nuclear energy; molten salt; molten salt fast reactor; chloride molten salt fuel; isotopic effect; reactivity; enrichment

## 1. Introduction

Molten salt reactors are currently seen as one of the most promising innovative reactor technologies with the potential to create an integrated, closed fuel cycle to assure resource security while producing future sustainable, see Merk et al. (2019) [1], say, potentially renewable, as suggested by Degueldre et al. (2019) [2], energy for future generations on wide scale and for advanced energy applications, see Roper et al. (2022) [3]. In recent years flowing fuel Molten Chloride Fast Reactors (MCFRs) have regained interest e.g. Merk et al. (2019a) [4], Mausolf, et al. (2021) [5], Krepel & Kramer (2021) [6], Serp et al. (2014) [7]. The use of natural chloride as molten salt anion has been originally promoted for these MCFR using for example NaCl-UCl<sub>4</sub>-UCl<sub>3</sub> as carrier salt and fuel salt with stable tetravalent/trivalent uranium chloride species as reported by Martinot (1982) [8] in LiCl-KCl and NaCl-KCl eutectics for example. Most of the R&D has been carried out on natural chloride. However the use of natural chloride (75.77% <sup>35</sup>Cl and 24.23% <sup>37</sup>Cl) induces specific ecological and neutron economical issues which need to be identified and solved.

Recently, Merk et al. (2019a)[3] for iMAGINE (U MSFR) and He et al. (2020) [9] for the thorium MCFR investigated the effect of <sup>37</sup>Cl enrichment. Both molten salt reactors are adapted for breeding, transmutation and fission of transuranic isotopes. The neutron absorption cross section of <sup>35</sup>Cl being

greater than for  $^{37}\text{Cl}$ , affects the MCFR neutron economy of the core. With on-line refuelling and in-line reprocessing/salt clean-up, the influences of  $^{37}\text{Cl}$  enrichment on neutron economy, breeding performance, and the production of harmful nuclides were analysed by He *et al* (2020)[8] in detail. Both groups showed that  $^{37}\text{Cl}$  enrichment has a strong impact on the neutron economy of a MCFR in initial criticality as well as in the breeding performance and long term operation. In addition to the absorption effect on reactor criticality, the in the use of natural chlorine, the yields of S isotopes and  $^{36}\text{Cl}$  are very high. An enrichment of  $^{37}\text{Cl}$  to 97% brings a valuable improvement of the neutronics during Th MCFR operation.

Historically, a centrifuge was the first device to separate the chlorine isotopes. This methodology was first used in 1934 by Jesse Beams from University of Virginia to separate  $^{35}\text{Cl}$  from  $^{37}\text{Cl}$ . This has been the best method for separating isotopes of elements, however other physical as well as chemical techniques were developed and are currently used today e.g. see Gosling (1999) [10].

The **physical isotope separation** methodologies considered here are fractionated distillation, mass spectroscopy, gas diffusion and **gas** centrifugation.

The **chemical isotope separation** techniques are partitioning on solid or liquid ion exchangers, chromatography, photochemical techniques and to complete, electrochemical based techniques (electro-migration and electrolysis **in solution or in molten salt**).

Chlorides in the molten salt has been identified as suitable (less scattering) for the molten salt **fast** reactor (MSFR) using for example  $\text{NaCl-UCl}_4\text{-UCl}_3$ . Most of the R&D has been carried out on natural chloride. However, the use of natural chloride (75.77%  $^{35}\text{Cl}$  and 24.23%  $^{37}\text{Cl}$ ) induces ecological and economical issues.

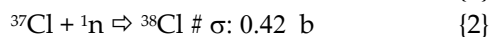
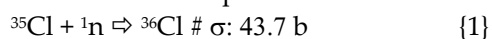
A significant ecological issue is the production of  $^{36}\text{Cl}$  by neutron activation of  $^{35}\text{Cl}$ . The isotope  $^{36}\text{Cl}$  is a soluble long live nuclide that makes it a 'first nuclide' in the safety assessment of the repository. Separation factor is investigated for gas centrifugation, distillation, chromatography and electrolysis.

This study revisits the **neutronics** data for a classical U MCFR, give reactivity and  $^{36}\text{Cl}$  results as a function of burn-up. It identifies the induced economical and ecological effects. A chlorine isotope separation technique is required for reducing the amount of  $^{36}\text{Cl}$  in the MCFR core. It subsequently reviews the isotopic properties and **isotope separation** methodologies that are physical or chemical. This study guides to identify techniques that could be used for the production of tons of  $\text{Na}^{37}\text{Cl}$  with a  $^{37}\text{Cl}$  purity of say 97-99%.

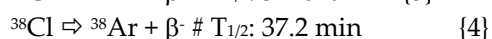
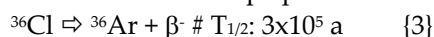
## 2. Neutronic

During irradiation, the chlorine isotope build-up and decays are described by capture followed by beta ( $\beta^-$ ) decays.

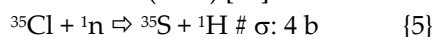
The chlorine isotope activation reactions are:



These chlorine isotope productions are followed by beta decay ( $\beta^-$ ) reactions:



producing in both cases Ar stable isotopes. Now with fast neutron  $^{35}\text{Cl}$  reacts producing  $^{35}\text{S}$  according to Gooden et al. (2018) [11]:



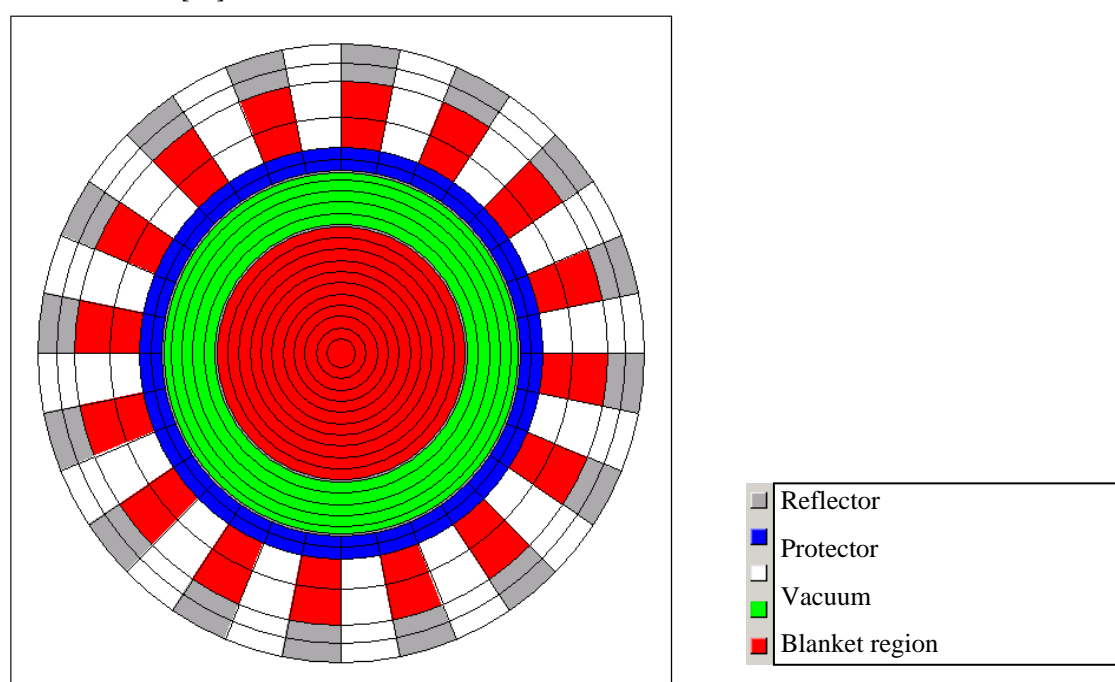
Criticality is consequently modified which affect reactivity and energy conversion yield.

### 2.1. Code, Model and Methods

For the simulations, the HELIOS code system versions: HELIOS 2.03 with the internal 173 cross sections group library [12] (based on ENDF/B 7.1). The code is a 2D spectral code with wide unstructured mesh capabilities and a transport solver, based on the collision probability method [13] and a newer extension based on the Method of Characteristics [14]. The general model is based on the EVOL benchmark configuration which is transferred to a volume corrected 2D HELIOS model

(see Figure 1). The model has been adopted for an as close as possible reproduction of the 3D structure and the relations between the different materials. Furthermore, the benchmark model has been extended to represent in addition the outer structures, the 16 heat exchanger pipe arrangement for a better representation of the real geometry. The leakage in the third dimension is introduced into the calculation through the insertion of a buckling correction available in HELIOS (BSQ: 0.00002). This value has been fixed by a comparison of 2D and 3D calculations within the EVOL benchmark exercises, see [15]. Using this setting a  $k$  of  $\sim 1.005$  is required for a pseudo 3D  $k_{\text{eff}}$  of 1.0. The leakage in radial direction is directly modelled through vacuum boundary conditions.

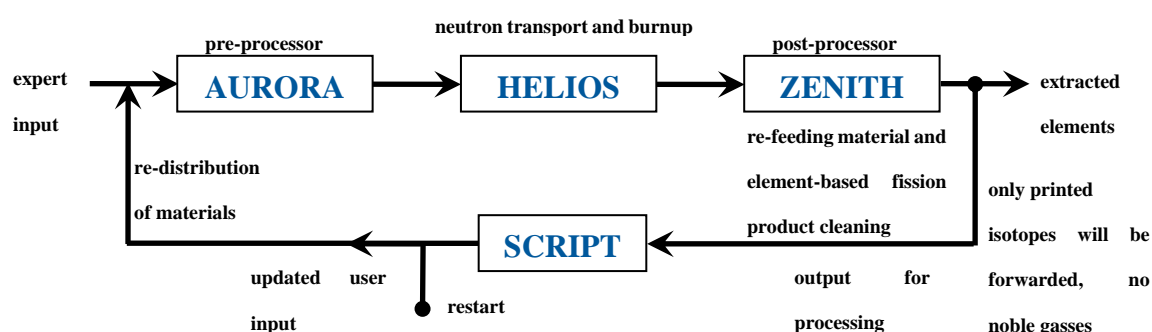
The salt system chosen for iMAGINE is based on NaCl-UCl<sub>3</sub>-UCl<sub>4</sub> with the eutectic composition 42.5mol%–17.0mol%–40.5mol%, more detailed discussion of the data of the salt system and the ratio behind the choice is given in Merk et al. (2019) [1]. For the reference case the carrier salt is based on the natural chlorine composition (76% <sup>35</sup>Cl and 24% <sup>37</sup>Cl), while the chlorine for the uranium salt is 99% enriched. The core size of model has been adopted to a radius of 213 cm and a <sup>235</sup>U enrichment of 11.06%. The used data is based on the results of two earlier studies [16,17] based on SCALE/POLARIS [18].



**Figure 1.** Volume corrected 2D HELIOS model of the molten salt reactor. Conditions: core (hot) radius of 213 cm, <sup>235</sup>U enrichment of 11.06%, second layer of fuel (cold) returning in core.

The HELIOS code is an industrial standard software which is designed to perform the neutron transport calculation, the burn up calculation, and if requested the cross section preparation in the whole system or in defined calculation areas under the consideration of the boundary conditions set for the unit cell. Originally, the HELIOS code has been written for the simulation of solid structured fuel assemblies, thus the possibility of online refueling and online reprocessing is not foreseen. To deal with these special features required for the simulation of molten salt reactors a PYTHON script has been developed by Merk et al. (2019) [3], which is based on the special features of the HELIOS package. All input data, which does not change during the whole reactor operation, is stored in a so-called expert input. The changing material configuration is fed into the system through a user input which is re-written in every cycle using a PYTHON script. Within each of the cycles 5 burnup steps are calculated through HELIOS. The expert input and the updated user input are merged in the pre-processor AURORA [13], which creates the updated input for the HELIOS run used for the determination of the neutron flux distribution and the burnup of the materials. The results are finally evaluated at the end of each cycle in the post-processor ZENITH [14]. On the one hand, it is decided here which elements are reduced or increased to which extent, and on the other hand, which isotopes

will be fed back into the next, new user input which is created with the help of the PYTHON script (see Figure 2). Theoretically, it would be possible to simulate a molten salt reactor precisely by using small time steps in this calculation loop. In a real MSR two different time scales for the salt cleanup can be observed, based on two different processes, the helium bubbling for gaseous and volatile fission products with a comparably short acting time, and the online salt cleanup for the dissolved fission products with a significantly longer acting time. To improve the modelling of both procedures a new strategy has been developed, based on the use of a reduced burnup per cycle (10 GW d t<sup>-1</sup> of HM using five burnup steps in HELIOS), coinciding with a full removal of gaseous and volatile fission products the elements 18 (Ar), 35 (Br), 36 (Kr), 53 (I), 54 (Xe), are not carried forward through ZENITH), while the dissolved fission products can be removed, based on a cleaning efficiency providing the opportunity to set this efficiency elementwise for all considered elements.



**Figure 2.** Description of the calculation cycle for MSR based on the HELIOS package.

The use of the described process has already been validated and used in several peer-reviewed publications Merk et al. (2020) [19] and Jessee et al. (2014) [20]. However, the modelling and simulation quality will be significantly improved due to the new code version and the increased computational power which allow now the use of the 173 energy group cross section set instead of the 47 group set in the earlier publications.

However, due to the characteristics of HELIOS, some approximations still have to be accepted. There is no fuel salt movement, thus an undesired burnup distribution arises during each of the calculation cycles, while the materials are only re-distributed when a new user input is defined. HELIOS is a LWR code and a LWR spectrum is used for the weighting of the master libraries inside each energy group. However, this error will be significantly reduced compared to earlier publications, since the number of energy groups is tripled, thus the width of each energy group has significantly reduced. Comparisons with other codes in the EVOL benchmark, in a fast reactor isotope accumulation test against SERPENT Merk et al. (2015) [21], as well as comparisons with SCALE/POLARIS see Merk et al. (2015) [22] have shown good agreement. This is what is currently available, finally to judge the reliability of the results, a real reactor physics experiment for molten salt reactors would be required as discussed in [1].

The approximations and the use of the HELIOS code package seem to be adequate for the approximation level required for this kind of long term investigation of isotope accumulation to support the development of a clean-up system. The results of the influence of different element on the system criticality has been evaluated against earlier publications Merk & Litskevich (2018) [23] Rachamin et al. (2013) [24]. It is here important to recognize that HELIOS was validated in the EVOL benchmark [23], but this benchmark was for Fluorine based salt.

The accumulation of isotopes is evaluated through a row of calculations of the system using the described dynamic calculation which incorporates the effect of the removal of the gaseous and

volatile fission products as given above. All other fission products are left in the system and the accumulation is observed in 10 GW d t<sup>-1</sup> of HM steps.

## 2.2. Neutronic Results

The first investigation of the effect of <sup>37</sup>Cl enrichment has identified very strong differences in the criticality effect. In any case the change from natural chlorine (75.77% <sup>35</sup>Cl and 24.23% <sup>37</sup>Cl) to 99% enriched <sup>37</sup>Cl leads to a strong increase in criticality.

The results point to a gain of ~4500 to ~10500 pcm which is an astonishingly large difference between industrially applied codes which are all based on the same cross section library ENDF/B VII.1. However, it should not be forgotten that the calculation of a chlorine based molten salt reactor is clearly outside of the validation based of each of the codes. The differences clearly demonstrate the demand for an experimental investigation of the problem to create a reasonable database for code validation. In addition, it would be of high importance to create a benchmark to investigate the differences in more detail with a wide set of codes.

It has to be recognized here, that the differences appear in the preparation of the master library for the codes or in the codes itself, most probably in the unresolved resonance treatment. Eventual uncertainties in the cross section libraries as already pointed out in literature regarding the issues with Cl-35 cross section and the efforts that have been made to measure (n,p) and (n,γ) cross section in the fast energy range, e.g. [25,26] will come on top or in a lucky incident will lead to error cancellation. Based on this two-fold recognition we would recommend on the one hand differential cross section measurements as already pointed out by in assessment of nuclear data needs for advanced reactor demonstrations, by Palmiotti, et al. (2021) [27], but on the other hand an integral reactor experiment, e.g. by using a pile oscillator, to provide a first reliable validation base for the code developers. These results will be required to improve e.g. the unresolved response treatment in the cross section preparation for the master library of deterministic codes or for determining/improving the p-tables for Monte-Carlo calculation.

The results of the dynamic calculation using HELIOS (Figure 3) show the effect of changing the <sup>35</sup>Cl content from natural chlorine configuration to the reference case (NaCl based on natural Cl, and UCl<sub>x</sub> based on 99% enriched <sup>37</sup>Cl), and the case with all chlorine in the reactor enriched to 99%. The steps in the curves indicate the different calculation cycles within the script with a set of classical burnup calculations within HELIOS, each to 10 GWd t<sup>-1</sup> of HM, and the change in criticality due to the removal of fission products and the refill of the fertile material, i.e. depleted U (0.3% <sup>235</sup>U), with constant U contents (balance) through the script at the end of each 10 GW-d t<sup>-1</sup> of HM step. In this configuration the general shape of the reactor behavior over burnup is not significantly changed, but it should be kept in mind that the criticality in the calculation is adopting the neutron source to get keep the calculation critical.

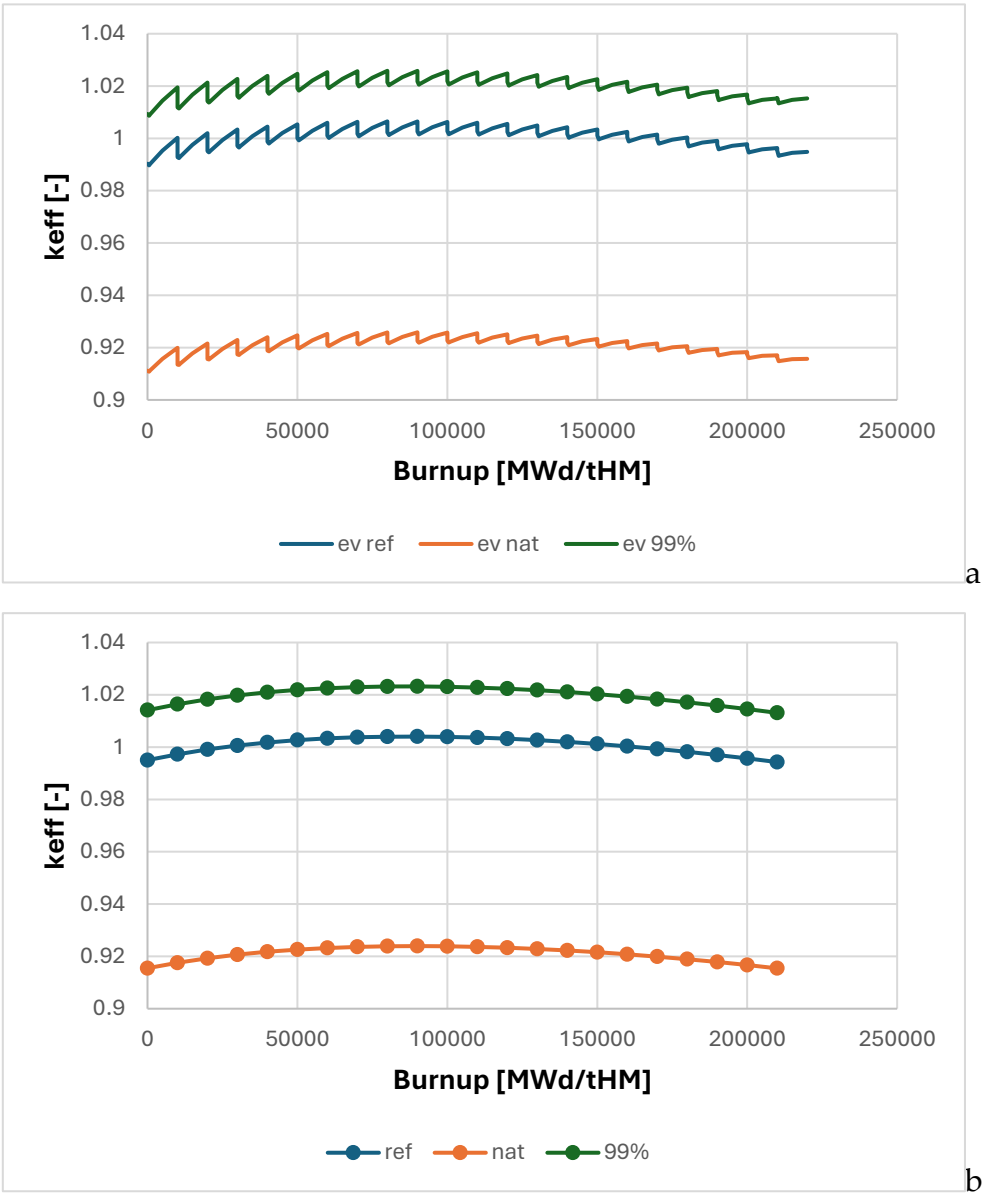
To ease the interpretation of the results all following investigations are based on the evaluation of the averaged criticality per cycle in the script as given in **Figure 2**.

To overcome the limitation of the criticality normalization of the first calculations, the next step will be to adopt the fissile material enrichment to get all cases to the same starting point which has been used in earlier studies to evaluate long term operation with breeding and the boundary condition that the criticality should be kept between ± 500 pcm around criticality as given in the reference case in **Figure 3**.

This reference case has an initial enrichment of 11.05% <sup>235</sup>U. For the case with natural chlorine an enrichment of 13.29% would be required to create the same starting criticality, while for the completely 99% enriched <sup>37</sup>Cl case only 10.58% <sup>235</sup>U enrichment would be required.

However, obviously not only the initial criticality is heavily influenced by the <sup>37</sup>Cl enrichment, but also the breeding behaviour, see **Figure 4**. The 99% enriched case provides clearly improved breeding and would achieve without further salt clean up about 50% longer reactor operation than the reference case, while the case using natural chlorine is not able to breed at all. There is no increase in criticality which would indicate proper breeding. This can be explained with the significant loss of

neutrons in absorption reactions in  $^{35}\text{Cl}$ , which clearly reduces the number of neutrons available for breeding.

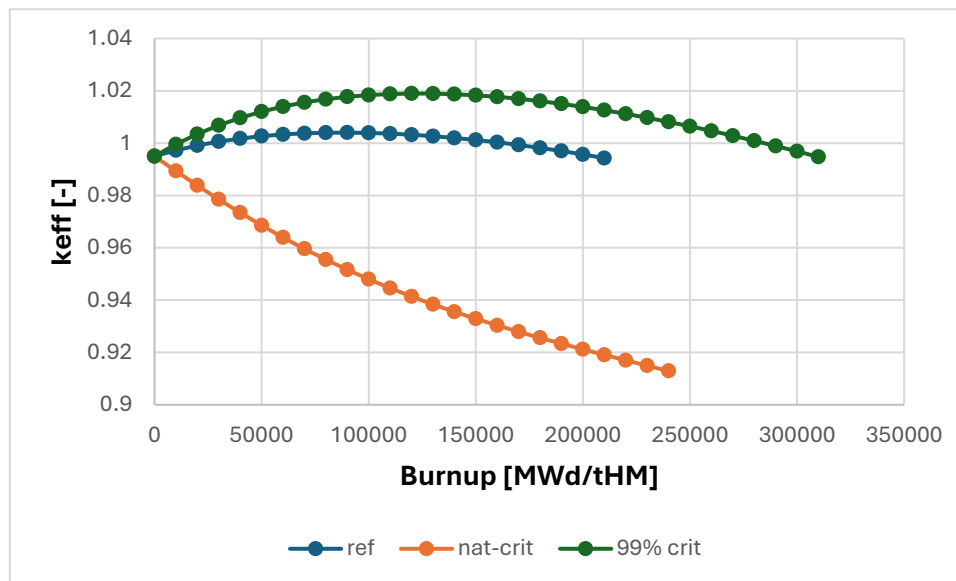


**Figure 3.** Development of the dynamically calculated criticality over burnup for different contents of  $^{35}\text{Cl}$  in the carrier and the fuel salt with explicit documentation of the cycle behaviour showing the steps of the HELIOS calculations as well as the steps of the script cycles.

.a. change in criticality due to the removal of fission products and the refill of the fertile material through the script at the end of each 10 GWd/tHM step.

.b. evaluation of the averaged criticality per cycle in the script as given in with one burnup averaged value per cycle initiated

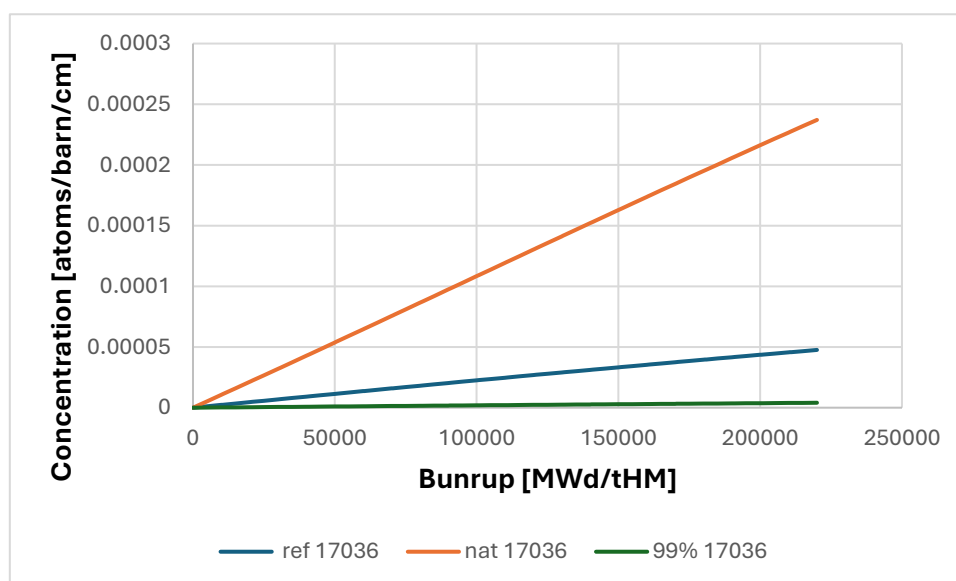
Conditions: core of 213 cm radius, fuel of  $\text{NaCl-UCl}_4\text{-UCl}_3$  composition with a  $^{235}\text{U}$  enrichment of 11.06%.



**Figure 4.** Cycle averaged development of the dynamically calculated criticality over burnup for different isotopic fraction of  $^{37}\text{Cl}$  in the carrier and the fuel salt, all cases adopted to the same starting value by changing the initial  $^{37}\text{Cl}$  enrichment of the uranium based fuel from natural isotopic composition through the reference case and to 99%.

The analysis of the  $^{36}\text{Cl}$  formation (**Figure 5**) indicates exactly the expected effect of neutron absorption in  $^{35}\text{Cl}$  leading to  $^{36}\text{Cl}$ . This effect is significantly stronger in the case natural chlorine is used. It leads to a  $^{36}\text{Cl}$  formation which is by a factor of ~5 higher than for the reference case. A 95%  $^{37}\text{Cl}$  enrichment reduces  $^{36}\text{Cl}$  content by a factor of 12, a 99% enrichment reduces the  $^{36}\text{Cl}$  content by a factor of ~60 and 99.9%  $^{37}\text{Cl}$  reduces the content by a factor of ~600. Comparison with  $^{129}\text{I}$  build-up, another 1st nuclide for the radioactive waste management may be suggested; however, iodine-129 build-up will be independent of the  $^{37}\text{Cl}$  enrichment. In conventional reactor fuel, the problem of  $^{36}\text{Cl}$ , which is only an impurity however, the influence in the final disposal studies, e.g. Renn (2013) [28], is almost as big as the effect of  $^{129}\text{I}$  which has a considerable fission yield. In our case we speak about much larger amounts of  $^{36}\text{Cl}$  which would be produced.

However, the problem is not only the loss of neutrons, it should always be kept in mind that  $^{36}\text{Cl}$  is a very long lived isotope which is currently seen as one of the challenging isotopes in the final disposal scenarios delivering a significant contribution to the release risk for the site. Thus, there are two good reasons for the  $^{37}\text{Cl}$  enrichment, the neutron economy as well as the waste management of fuel when it is taken out of the reactor.



**Figure 5.** Development of the dynamically calculated  $^{36}\text{Cl}$  concentration over burnup for different contents of  $^{35}\text{Cl}$  in the carrier and the fuel salt.

### 3. Isotope Separations

There are basically three types of isotope separation techniques; they are

- based directly on the atomic weight of the isotope,
- based on the small differences in chemical reaction rate, and,
- based on properties such as spectroscopic not directly connected to atomic weight.

The third type of separation is mostly experimental. All practical separation techniques depend in some way on the atomic mass. It is therefore generally easier to separate isotopes with a larger relative mass difference. However, with chlorine and because of its strong reactivity it has the tendency to join with its self or with more or less electronegative elements or molecules, or, with other (lighter or heavier) elements or molecules associated that must be considered in the separation. They are important in isotopic separation, however two isotopes can exchange between two phases according to:



with El an element. The molecule ClEl can then be HCl, LiCl, Cl<sub>2</sub>, ICl, CsCl or CH<sub>3</sub>Cl as example.

The yield of the separation process is generally quantified using the separation factor  $\alpha_{37/35}$  defined as

$$\alpha_{37/35} = 1 + \varepsilon_{37/35} = k_{37\text{Cl}}/k_{35\text{Cl}} \quad (1)$$

Where  $\varepsilon_{37/35}$  is the separation yield and  $k_{35\text{Cl}}$  is the retention factor. Isotopic effects allow the separation, which is physical or chemical, e.g. see Bigeleisel (1969) [29].

#### 3.1. Physical Separations Methods

Centrifugation was the first method **invented** to separate chlorine isotopes by Beams [30]. He separated successfully  $^{35}\text{Cl}$  from  $^{37}\text{Cl}$  in 1937. The electromagnetic method uses a mass spectrometer, or spectrograph, to send a stream of charged elemental particles through a strong magnetic field and allow the separation of isotope by mass.

In gaseous diffusion molecules of a lighter isotope would pass through a porous barrier, and become isolated from those of a heavier isotope. Separation has also been carried out by fractionated distillation

Separation by Fractionated Distillation...

The separation method is based on the difference between the partial pressure  $P_{\text{ClE}}$  of molecular constituent  $^{35}\text{ClE}$  and  $^{37}\text{ClE}$ . The separation factor  $\alpha$  is simply given by the expression:

$$\alpha_{37/35} = P_{^{37}\text{ClE}} / P_{^{35}\text{ClE}} \quad (2)$$

The distillation of chloroform, carbon tetrachloride, methyl alcohol, and benzene were found e.g. Baertschi et al. (1953) [31] to lead to an enrichment of  $^{35}\text{Cl}$  in the distillate, whereas the other heavy isotopes such as  $^{37}\text{Cl}$  and  $^{18}\text{O}$  were enriched in the still pot. A possible general rule is suggested that in isotopic molecules having a central atom, the molecular variety containing the heavier isotope of the central atom will exhibit a somewhat higher vapour pressure than the variety containing the lighter isotope as the central atom. However rules have exceptions...

With  $P_{\text{ClE}}$  the partial pressure of  $^i\text{ClE}$ , Liebscher et al. (2006) [32] measured experimentally the chlorine isotope fractionation between vapour and liquid in the system  $\text{H}_2\text{O}-\text{NaCl}$ . Experiments were performed on the  $400^\circ\text{C}$  isotherm between 23 and 28 MPa and on the  $450^\circ\text{C}$  isotherm between 38 and 42 MPa. Calculated chlorine isotope fractionation  $\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = \delta^{37}\text{Cl}_{\text{vapor}} - \delta^{37}\text{Cl}_{\text{liquid}}$  ( $1\sigma = \pm 0.17\text{‰}$ ) between the coexisting vapour and liquid are generally within 0.2‰ of 0, although there is a trend at both  $400^\circ\text{C}$  and  $450^\circ\text{C}$  in which the  $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$  values change with pressure beyond statistical uncertainty.

### Separation by Electromagnetic Separation

Mass spectrographic method has been used by Sun et al. (2014) [33] in the determination of chlorine (Cl) isotopes in various substrates. The procedure includes sample treatment, three-step ion chromatographic separation of Cl isotopes, and isotope ratio determination based on  $\text{Cs}_2\text{Cl}^+$  ion in positive thermal ionization mass spectrometry. The recovery of the method and the fractionation of Cl isotopes were validated using certified reference standard materials. The pre-treatment strongly eliminated the effects of organic impurities and other anionic interferences, especially soluble nitrates and sulphates.

Inductively coupled plasma mass spectrometry (ICP-MS) may be use for the analysis of cations or anion in solution e.g. Degueldre (2017) [34]. Chlorine isotopes as well as bromide and iodine and metals content can be measured by ICP-MS in drinking water as reported by Quarles Jr. et al. (2020) [35]. These ICPMS isotope separations concern however very small amount of material.

### Separation by Diffusion

For two isotopic molecules, diffusion speed ( $v$ ) ratio ( $\rho$ ) is given by ...

$$\rho_{37/35} = v_{^{37}\text{ClE}} / v_{^{35}\text{ClE}} = (\mu_{^{35}\text{ClE}} / \mu_{^{37}\text{ClE}})^{1/2} \quad (3)$$

The lighter is the faster. Effects of mass and of size must be reported.

Kranz & Watson (1953) [36] performed successfully chlorine isotope separation by thermal diffusion. The thermal diffusion constant of HCl has been determined to be +0.010 at  $T_r = 685\text{ K}$  and -0.009 at  $T_r = 229\text{ K}$ . Such a rapid change of  $\alpha_{37/35}$  and  $RT$  with temperature and an inversion temperature at or above room temperatures seem to be characteristic of strongly polar molecules. The troublesome "memory effects" of HCl in a mass spectrometer can be eliminated by using a pin-hole leak right in the box of the ion source plus a baking out, flushing and repeated-analysis routine. Some details are given of a 6.8-meter hot-wire thermal diffusion column apparatus, having an equilibrium separation factor of 7, and which has provided fairly large samples of HCl enriched to 94%  $\text{H}^{35}\text{Cl}$  and 62%  $\text{H}^{37}\text{Cl}$  for cyclotron beam targets and other experiments.

### Separation by Gas Centrifugation

The gas centrifuge works on the principle of partial pressure ( $p$ ) diffusion, e.g. Kemp (2009) [37]. The centrifuge accelerates gas molecules toward the rotor wall of radius  $r$ . A counteracting diffusive force created by the thermal motion ( $RT$ ) of the molecules seeks to distribute the gas evenly throughout the rotor volume. The two forces balance through a dynamic equilibrium, which gives rise to a pressure distribution in the rotor that is a function of the molecular mass ( $M$ ) of the gas:

$$p^{\text{A}}\text{Cl}(r) = p^{\text{A}}\text{Cl}(0) \exp\{M(\text{A}^i\text{Cl}) \omega^2 r^2 / 2R T\} \quad (4)$$

for the isotope A and the partial pressures  $p^A\text{Cl}(r)$ .

Dividing the two equations gives a simple separation factor for the centrifuge, which is a function of the mass difference and the peripheral velocity:

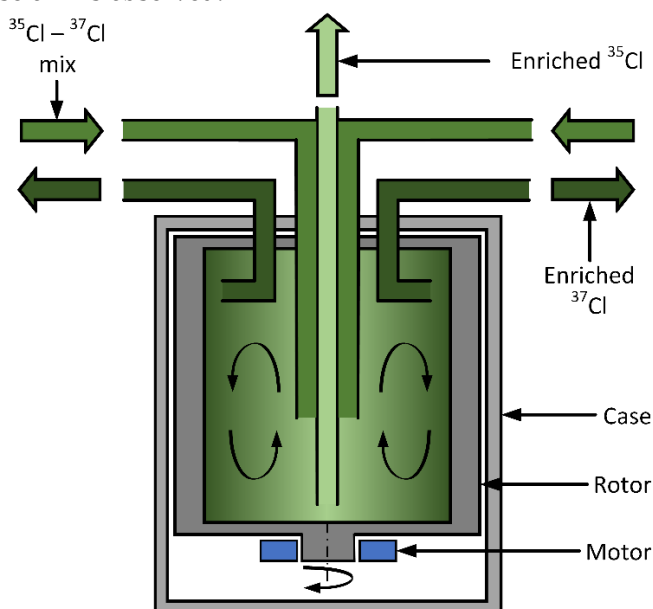
$$\alpha_{0,37/35} = \{[pA(0)/pB(0)] / [pA(r)/pB(r)]\} = \exp\{[M(^{37}\text{Cl}) - M(^{35}\text{Cl})] \omega^2 r^2 / 2R T\} \quad (5)$$

Equation (4) is valid in the equilibrium conditions where the gas is stationary in the reference frame of the rotor and enough time has passed that the molecules have diffused into their final distribution. However, the performance of a centrifuge can be enhanced by introducing a counter-current flow, in which the gas flows up the centre axis of the rotor and back down along the rotor wall.

Study of isotope separation of some chemical elements in a gas centrifuge was also investigated by Aisen et al. (1996) [38]. Effect of a field on isotope separation is described by the separation factor given by:

$$\alpha_{0,37/35}^0 = \exp -(\Delta M_{37/35} v^2 / 2RT) \quad (6)$$

$\Delta M$  molar mass difference ( $\text{kg mol}^{-1}$ ) and  $v$  the gas linear speed of displacement ( $\text{m s}^{-1}$ ). The light isotope atoms (or molecules) concentrate in centre of rotor and the heavy in periphery. A schematic of a gas centrifuge is shown in **Figure 6**. The separation factor of  $^{37}\text{Cl}/^{35}\text{Cl}$  is plotted **Figure 7** a function of the linear speed  $v$  and of the temperature  $T$ . The increase of the separation factor  $\alpha$  with  $v$  is strong and its increase with a decrease of  $T$  is observed.



**Figure 6.** A schematic of a gas centrifuge unit during  $^{37}\text{Cl}$  separation from  $^{35}\text{Cl}/^{37}\text{Cl}$  gas mix.

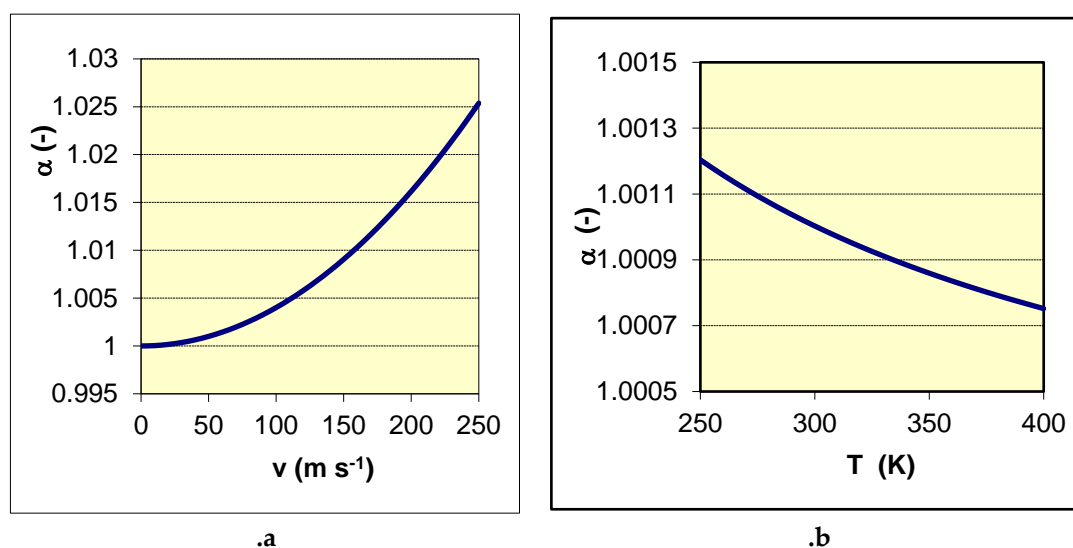
Actually, the simplified linear centrifugation model used in Equations (4)–(6) assumes no gas centrifugal-force-assisted diffusion of species, which leads to a quasi-equilibrium model that assumes that partial pressure of isotopes goes instantaneously to equilibrium. This assumption is not accurately valid as the enrichment of  $^{37}\text{Cl}$  over  $^{35}\text{Cl}$  is higher, since the effective diffusivity of  $^{37}\text{Cl}$  is impeded by the larger  $^{35}\text{Cl}$  content. The separation assumptions may then be complemented by a time-dependent diffusion model for centrifugal separation such as presented by Bogovalov (2015) [39].

The separation factor (for molar weight difference),  $\alpha_0$ , depends on many variables, see Ying et al. (2006) [40], including

construction parameters of the centrifuge unit,

- length of the gas centrifuge
- radius of the centrifuge
- axial location of the feed point
- parameters of the scoops
- operational conditions

- feed flow rate,
  - pressure at the wall and on physical properties
  - peripheral rotation speed
  - feed rate of the working gas
  - temperature  $T_0$  at injection
  - temperature distribution on the wall
  - pressure of the gas at the rotor wall
- physical properties of the working gas, such as:
- molar weight of the isotope reagent
  - viscosity of the gas
  - molar weight of the carrier gas (if any)
  - product density media
  - product diffusion coefficient.



**Figure 7.** Separation factor of  $^{37}\text{Cl}/^{35}\text{Cl}$  as a function of  $v$  and of  $T$ . Conditions:  $\Delta M$ :  $2 \text{ g mol}^{-1}$  .a  $T = 300 \text{ K}$  .b  $v = 50 \text{ m s}^{-1}$  . Note the increase of  $v$  enhances strongly the isotope separation, a decrease of  $T$  increases slightly  $\alpha$ .

### 3.2. Chemical Separation Methods

The phase providing retention/separation may be a solid or a liquid. The yield of the separation process is generally quantified using the separation factor  $\alpha$  defined as

$$\alpha_{37/35} = k_{35\text{Cl}} / k_{37\text{Cl}} \quad (7)$$

Where  $k_{35\text{Cl}}$  is the retention factor of  $^{35}\text{Cl}$  in the  $^{35}\text{ClEI}$  form onto subtract.

#### Separation Using Solid Ion Exchangers

Ion exchanger separation is largely used for recovery of metal ions e.g. Musashi et al. (2007) [41]. In the late 70ies Heumann tested the separation of chloride isotopes using strongly basic anion exchangers contacted with aqueous  $\text{KF}$ ,  $\text{NaBF}_4$  and  $\text{NaNO}_3$  solutions at  $0$ – $60^\circ\text{C}$ , see Heumann & Baier (1980) [42]. These authors found that the separation factor of chlorine isotopes depends on the nature and concentration of the eluent in these ion chromatography tests. This factor value increases when the eluent salt concentration decreases.

Columns of hydrous zirconium dioxide particles, produced by hydrolysis of zirconyl chloride solution, were also tested by Heumann et al. (1980) [43] for isotope fractionation of chlorine. In separation experiments, using strong basic anion exchange, enrichment of  $^{35}\text{Cl}$  was found in the first fractions, whereas the last fractions showed higher concentrations of  $^{37}\text{Cl}$ . The isotope fractionation decreases when concentration increases. Using a  $0.5 \text{ M NaNO}_3$  solution the elementary separation effect was calculated  $\varepsilon = 6.1 \times 10^{-4}$  ( $\alpha = 1.00061$ ) as reported by Heumann & Baier (1980) [35].

The calculation of the break-through curve maybe easily performed for both  $K_{d35Cl}$  and  $K_{d37Cl}$  the break though curve see Figure 8a.

Chlorine isotope fractionation factors were also determined by strongly basic anion-exchange chromatography with 0.1 M HCl at 25°C by Musashi et al. (2004) [44]. The magnitude of the factor was calculated as a single-stage separation factor of 1.00030 with analytical precision of 0.00006 (1 $\sigma$ ). The tests demonstrated that the **light isotope was preferentially adsorbed** into the resin phase, while the heavy one ( $^{37}Cl$ ) enriched in the solution. This discrepancy is due isotope effect accompanying hydration rather than an isotope effect due to a phase change Musashi et al. (2007)[34].

### Separation Using Liquid - Liquid Extraction

Liquid - liquid extraction has been used successfully for the separation of isotopes. Here, for the partitioning of ClEI between 2 liquids ( $L_1/L_2$ ) the separation factor equals:

$$\alpha_{37/35} = \{ [^{37}ClEI]/[^{35}ClEI] \}_{L_1} / \{ [^{37}ClEI]/[^{35}ClEI] \}_{L_2} \quad (8)$$

The organic liquid film extraction system has been investigated for the extraction and separation of lithium isotopes using ionic liquid as diluent and Dibenzo-15-crown 5-Ether as the extractant, see Zhang et al. (2020) [45] The authors investigated, the effects of extraction time, the gas flow rate, the temperature, the counter anions of lithium salt, the length of the cationic carbon chain of ionic liquid on extraction, and the separation of lithium isotopes. The maximum separation factor  $\alpha$  was  $1.037 \pm 0.002$  and the abundance of  $^6Li$  increased from 7.61 to 7.86%.

The values of the single stage separation factor  $\alpha$  are  $1.0067 \pm 0.0035$  and  $1.025 \pm 0.005$  and are close to similar values for rectification of boron trifluoride as reported by Khoroshilov & Ivanov (2018) [46].

Chlorine isotope separation by liquid-phase thermal diffusion has been tested successfully by Rabinovich & Ivakhnik, (1978) [47], reporting a factor  $\alpha$  of  $1.2 \pm 0.1$  for chlorine isotope separation from  $CCl_4$ ; a factor  $\epsilon_{37/35}$  of 0.2 was determined using trichloroethylene and in butyl chloride. While, in gaseous isotopic mixtures this value, as a rule, does not exceed 0.02.

### From the Solid - Liquid to the Liquid - Liquid Extraction

The breakthrough by elution through a sorbing/porous column can typically be estimated on the basis of the retardation factor,  $R$ , using the relationship:

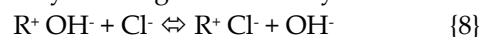
$$R_{Cl} = 1 + (\rho K_d(Cl^-))/\xi \quad (10)$$

with  $K_{dCl}$  the partitioning coefficient of the chloride isotope,  $\rho$  the density of this adsorbing material and  $\xi$  the porosity of the partitioning phase or  $V_w/(V_w+V_{ab})$ , with  $V_w$  the volume of water and  $V_{ab}$  the volume of absorbent for a given segment of column, when using coating solid or liquid, porosity

The separation factor between the 2 isotopes can be evaluated using:

$$\alpha_{37/35} = R_{37Cl} / R_{35Cl} \quad (11)$$

As anionic extraction/exchanger reagents, e.g. Nesterenko (2019) [48], the amines (e.g.  $R^+ OH^-$ ) are well known to easily exchange their  $OH^-$  by  $Cl^-$ . The reaction guiding this exchange write:



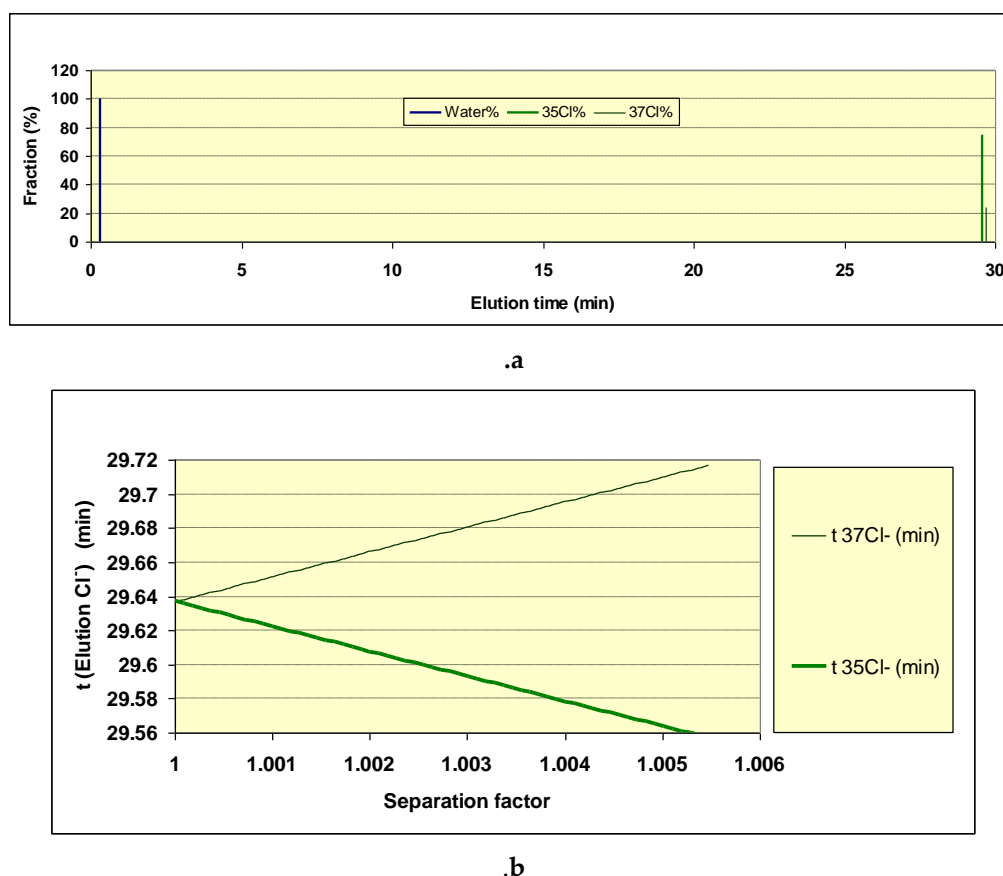
.and its equilibrium constant reads:

$$K(Cl^-/OH^-) = \{ [R^+ Cl^-] [OH^-] \} / \{ [R^+ OH^-] [Cl^-] \} \quad (12)$$

Its value for natural  $Cl^-$  is 22, Ref Bio-Rad (2023) [49]. On the basis of the  $K_{id}$  definition, one can write that

$$K(Cl^-/OH^-) = K_d(Cl^-)/K_d(OH^-) \quad (13)$$

.with  $K_d(OH^-)$  postulated to 1 then we obtain  $K_d(Cl^-) = 22$ . Now for  $K_d(^{35}Cl^-) = 22.1$  and  $K_d(^{37}Cl^-) = 21.9$  (indicative values) one can calculate the breakthrough and the retardation factor for each isotope, see Figure 8. The breakthrough and separation of  $^{35}Cl$  and  $^{37}Cl$  during their elution in capillary column is also plotted in Figure 8 for their  $\alpha_{37/35}$  values.



**Figure 8.** Breakthrough of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  during their elution in capillary column,.

**a.** separation for  $\alpha = 1.0020$ ,

**b.** effect of the separation factor from 1.000 to 1.005 on the peak splitting.

**Conditions:** column length 100 cm, internal radius 1 mm, adsorbent radius 2 mm, porosity 0.25, eluent water,  $v$ : 3 mL min $^{-1}$ ,  $K_d(\text{Cl}^-)$ : 22 mL g $^{-1}$ .

The basic theory of ion elution into ion exchanger (solid or liquid) column developed by van Deemter et al. (1956) [50]. The authors found that the separation performances may be described by the plate height theory. The van Deemter relationship relates the 'height equivalent of a theoretical plate' (HETP) associated to a chromatographic column to flow and kinetic parameters. These parameters cause consequently peak broadening with the Eddy-diffusion, the diffusion coefficient (resulting in dispersion of the eluted species), the mass transfer coefficient and the eluent velocity. For a coated capillary column, the Eddy-diffusion becomes 0 and peak enlargement reduces.

### Separation by Photochemistry

Historically, the first photochemistry tests on isotopic separation were carried on chlorine gas. Chlorine isotopes activate specifically. The excitation of  $^{35}\text{Cl}$  differs from that of  $^{37}\text{Cl}$  as reported by Kuhn & Martin (1932) [51]. One can consequently produce specific isotopic molecular species.

Kuhn et al. (1941 & 1942) [52] observed that on irradiation of  $\text{ClO}_2$  by ultra violet light (2816.1 Å), the  $\text{Cl}_2$  liberated a slight excess of  $^{35}\text{Cl}$ . The  $^{35}\text{Cl}/^{37}\text{Cl}$  ratio during the photochemical reaction passes from 3.41 to 3.57, unveiling the potential of this technique.

A similar approach, for chlorine isotope separation, has been used by Liu et al. (1975) [53] and by Zare (1976) [54]. Illumination of iodine mono-chloride at 6053 Å excites selectively  $\text{I}^{37}\text{Cl}$ . The same band of  $\text{I}^{35}\text{Cl}$  is about 15 Å away. The excited  $\text{I}^{37}\text{Cl}$  reacts with added 1,2-dibromoethylene to form the  $^{37}\text{Cl}$  enriched  $\text{ClHC=CHCl}$ . At this wavelength no photo-dissociation of  $\text{ICl}$  takes place.

### Electrolytic Separation

### Separation by Ionic Migration

Applying current in a long tube filled by agar-agar gel containing a salt NaCl makes the  $\text{Cl}^-$  zone migrate 3 months over 30 m in the gel. In the case of  $^{35}\text{Cl}^-$  and  $^{37}\text{Cl}^-$ , the  $\frac{1}{2}$  cells are respectively filled with NaOH (anodic  $\frac{1}{2}$  cell) and HCl (cationic  $\frac{1}{2}$  cell). Today glass powder is used instead of agar - agar to avoid convection. The light isotope concentrate at the anode and pass from 75.76% to 80.70%.

Separation of chlorine isotopes may be achieved with high resolution for chloride isotopes using capillary zone electrophoresis. The separation conditions are: capillary of 75  $\mu\text{m}$  diameter, 47 cm length,  $V = 20$  kV,  $T = 25^\circ\text{C}$ , electrolyte chromate/borate and pH 9.2, see Lucy & McDonald (1995) [55].

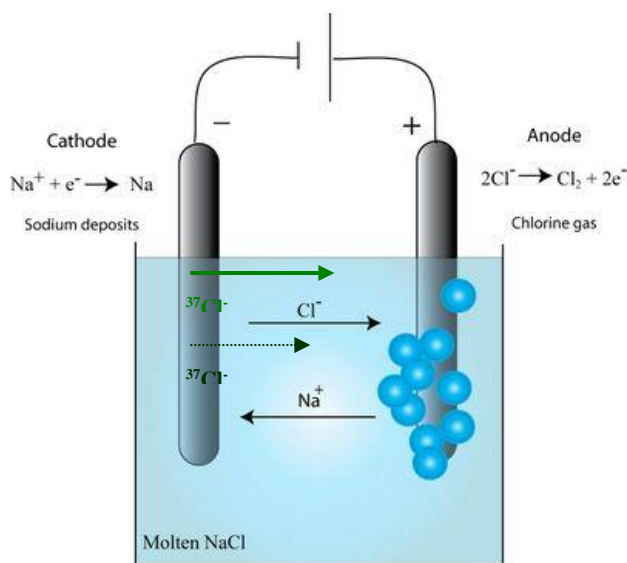
Similarly, electrolysis separation may be carried out. It includes ionic migration toward the electrode and electro-reaction at the electrode itself.

### Separation by Chloride Electrolysis

Electrolysis is known to be powerful for isotope separation. This is the case for  $^1\text{H}$  vs  $^2\text{H}$ , e.g. Petek et al. (1980) [56] as well as for  $^6\text{Li}$  vs  $^7\text{Li}$ , e.g. Wild et al. (2022) [57].

Klemm (1952) [58] suggested a system including a U tube, filled with 0.13 mm quartz powder the  $\frac{1}{2}$  cells are equipped with graphite electrodes. A review of the experimental methods of isotope separation by electrolytic migration. A theoretical explanation of the results in fused salts is developed. NaCl in **molten** salt form has been investigated at  $700^\circ\text{C}$ . The published experimental data for enrichment of cations in pure fused LiCl,  $\text{ZnBr}_2$ ,  $\text{ZnCl}_2$ , AgI,  $\text{CdCl}_2$ , and  $\text{TlCl}$  were compared with the theory and found to be in good agreement. Subsequently, Klemm & Lundén (1955) [59] investigated Cl isotope enrichment through electrolytic diffusion of  $\text{Cl}^-$  ions in **molten**  $\text{PbCl}_2$  with a solution anode made of molten Pb and with a current density of  $5\text{ A cm}^{-1}$  in 7 days. An enrichment of about 135 with a separation coefficient of 2 was recorded. The diffusion velocities of the  $\text{Cl}^-$  isotopes differ by  $(0.29 \pm 0.02)\%$ . The mass effect for electrolytic diffusion of chlorides is in molten  $\text{PbCl}_2$ :  $\mu = -0.052 \pm 0.003$ .

The model geometry and settings are based on a symmetric cell for electrolysis, see **Figure 9**. Two chlorine electrodes are separated by a liquid electrolyte e.g. NaCl horizontally. The left boundary was set as the cathode ( $\text{Cl}_2$  production), and the right boundary was set as the anode ( $\text{Cl}_2$  stripping). The cross-sectional area of the electrodes is  $1\text{ cm}^2$ . The temperature was  $298.15\text{ K}$ , and the total exchange current density at each electrode is  $1\text{ mA cm}^{-2}$ . Initially, isotope fractions in the  $\text{Cl}_2$  electrodes and electrolytes were the natural abundance ratio  $r_0 (= 75\%/25\% = 3.0)$ . This is equivalent to  $0.75\text{ M }^{35}\text{Cl}^-$ ,  $0.25\text{ M }^{37}\text{Cl}^-$ , and  $1\text{ M}$  cation in the liquid electrolyte. In the fluid phase, the **lighter** the isotope, the **faster** it moves.



**Figure 9.** The schematic diagram for electrochemical  $^{37}\text{Cl}$  enrichment in the fluid phase. After applying a constant current density to the cell, solid chloride is electro-generated into the anode

electrode (*left*) with a ratio of  $[^{35}\text{Cl}]/[^{37}\text{Cl}]$  greater than the original natural abundance of 3 as a result of isotope diffusivity.

Methodology may be derived from that developed by Wang et al. (2022) [60].

The electrode reaction {9} is as follows:



The electrode equilibrium potentials for  $^{35}\text{Cl}^-/^{35}\text{Cl}_2$  and  $^{37}\text{Cl}^-/^{37}\text{Cl}_2$  are governed by their own Nernst Equations at equilibrium (two separate redox reactions).

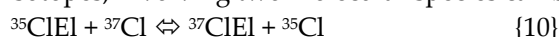
The electrolytic separation coefficient  $\alpha$  has been determined for the chlorine isotope separation in the electrolysis of sodium chloride solutions at a platinum anode by Johnston & Hutchison (1942) [61]. The separation factor was found rather independent on either temperature (25° to 40°C) or current density on **platinum** ( $1.0060 \pm 0.0005$ ) and was comparable with the value found on **graphite** ( $1.0068 \pm 0.0014$ ).

#### 4. Discussion

Isotope separation takes place in fluid phase where the isotopes form a mix in liquid or in gaseous phase. The isotopic separation performance is reduced by antagonism chemical or physical interactions such as isotopic exchanges, kinetic effect or mixing/convection.

##### *Isotopic Exchanges*

Isotopic exchanges, which are important antagonist interactions during isotopic separation of two isotopes, involving two molecular species can be written according to:



where El is an element that can be a metal, a non-metal or an organic group.

The equilibrium reaction is characterized by a constant,  $K$ :

$$K = ([^{37}\text{ClEl}][^{35}\text{Cl}]) / ([^{35}\text{ClEl}][^{37}\text{Cl}]) \quad (14)$$

When the exchange includes isotopes at two valence states, the heaviest isotope concentrates in the higher valence state. As an example for chlorine the following equilibrium has been studied e.g. Li & George (2005) [62]:



here  $K = 1.035$  and  $^{37}\text{Cl}$  concentrates in the  $\text{ClO}_4^-$  redox stage.

In the case of  $\text{Cl}_2$  exchange can also takes place. These reactions can clearly interfere with the separation. As an example for natural Cl the composition is 75.77%  $^{35}\text{Cl}$  and 24.23%  $^{37}\text{Cl}$  (monoatomic); however for  $\text{Cl}_2$  after isotopic exchange the following diatomic isotopic compositions of the diatomic gas are found: 63.05%  $^{35}\text{Cl}_2$ , 31.08%  $^{37}\text{Cl}^{35}\text{Cl}$  and 5.87%  $^{37}\text{Cl}_2$ , instead of 57.41%  $^{35}\text{Cl}_2$ , 36.72%  $^{37}\text{Cl}^{35}\text{Cl}$  and 5.87%  $^{37}\text{Cl}_2$ , for the natural composition.

##### *Kinetic Effects...*

A study of  $^{35}k/^{37}k$  for the elimination of hydrogen chloride (HCl) from ethyl chloride ( $\text{CH}_3\text{CH}_2\text{Cl}$ ) in gas-phase is reported by Christie et al. (1975) [63]. They found at 723 K that  $K$  is  $1.0015 \pm 0.0002$ . When considering the heavy atom kinetic isotope theory in an attempt to simulate the transition state, a moderate lengthening of the carbon-chlorine bond and a little motion of the chlorine atom gas are found.

More recently, Lewandowicz et al. (2001) [64] have found chlorine isotope kinetic effects during dehalogenation; the reaction is catalysed by an enzyme from *Xanthobacter Autotrophicus* and the  $k$  values reported are  $1.0045 \pm 0.0004$  for 1,2 dichloroethane and  $1.0066 \pm 0.0004$  for 1 chlorobutane.

The **single-stage** separation factor for chlorine isotopes ( $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ) was determined by Musashi et al. (2007) [65] to be 1.00034 by anion exchange chromatography. Here the separation is carried out on a 4.5-m column at 25°C. It was noted that the lighter isotope,  $^{35}\text{Cl}$ , was faster adsorbing on the resin, while  $^{37}\text{Cl}$  the heavier isotope was released into the aqueous solution. It must be noted that theoretical results on  $\text{Cl}^-$  isotope fractionation and the experimental results for Cl isotope separation during NaCl precipitation contradict the  $^{37}\text{Cl}$  isotope preferential enrichment into the solid

phase. This discrepancy is discussed based on the theory of isotope distribution between two phases. It is suggested that the chromatographic results reflect an isotope effect accompanying hydration and not an isotope effect driven by a phase change.

### *Convection and Mixing*

**Convection** is single or multiphase fluid flow that may be due to the combined effects of heterogeneities and forces in the bulk of fluid, usually density and gravity. When the cause of the convection is unspecified, convection due to the effects of thermal expansion and buoyancy can be assumed. Convection may also take place in soft solids or mixtures where particles can flow.

Improving the separation performance of the gas centrifuge can be a practical step in reducing enrichment costs e.g. Ghazanfari & Shadman (2022) [66]. For this purpose, it is necessary to accomplish a reliable convection–diffusion equation to predict the separation characteristics of the gas centrifuge. The species continuity equation is derived in the possible complete form and then solved with the finite volume method for a model rotor.

To **avoid isotopic mixing**, separation must be faster than the remix or turbulence effect.

Specifically the method for laser separation of chlorine isotopes includes irradiating a starting gas in the form of hydrogen chloride HCl with resonance infrared radiation with wavelength 3.782  $\mu\text{m}$ , subsequent exposure to laser radiation in the optical or infrared range, with intensity higher than  $10^{13} \text{ W cm}^{-2}$ , and extracting the formed positive ions, wherein the time between the exposure to resonance infrared radiation and laser radiation should not be longer than the decay time of the oscillatory state of hydrogen chloride HCl.

Basically electrolysis produces chlorine bubbles that during their growth move gas phase in the electrolyte solution mixing the isotopes.

### *From Single Stage to Multi-Stage Separation*

Single stage separation unit is affected by the size and geometry of the stage which are intrinsic parameter of the unit. Optimising the flow and the thermodynamic parameters ( $T, P$ ) affects the separation factor.

When the separation is not efficient enough with a single stage process, multi-stage or cascade approach may be needed. The space-time-concentration relationships of isotopes in an infinitely long separation tube, with end volumes, are calculated theoretically by Klemm (1948) [67].

Johns (2013) [68] showed that chlorine isotopes are separated by the electrolysis of molten zinc chloride over molten zinc electrodes. The chlorine generated at the anode reacts with liquid zinc to reproduce zinc chloride while zinc metal is transported from the anode to the cathode. Since  $^{35}\text{Cl}$  has a slightly faster migration rate than  $^{37}\text{Cl}$ , the former concentrate at the anode. The migration takes place in a small glass column. To suppress convection currents the column is filled with powdered glass. The column used for separating the chlorine isotopes was about 20 cm long, 5 mm in diameter which use to be common, see Klemm & Lundén (1955). Currents of 0.5 A at 130 V led to a separation factor of about 2, after about a week.

### *Combined Processes*

To complete the discussion it must be noted that combination of processes improve the separation. Some examples are given below.

### *Evaporation - Precipitation*

In nature coupling of evaporation and precipitation occurs. This contributes to local isotopic enrichments. The isotope separation of chlorine during brine evaporation has been reported by Luo, et al. (2012) [69] e.g. for saline lakes. Brine evaporated with complete fractionation and precipitation from brines by continuous precipitation during the evaporation. Samples of precipitate and brine were analysed for their  $\delta^{37}\text{Cl}$  values. The precipitates enriched with  $^{37}\text{Cl}$  relative to the brine samples,

and the  $\delta^{37}\text{Cl}$  of both the precipitate and brine samples decreased gradually during evaporation. The separation factors ( $\alpha_h$ ) between crystallised salt and brine were the highest.

Sorption - Volatilisation

Chlorine isotope separation during preparative capillary gas chromatography was studied by Holmstrand et al. (2006) [70] using 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane (DDT) as reference for semi-volatile organochlorine (OCl) compounds. Chlorine analysis by thermal ionization mass spectrometry showed no significant change of the chlorine isotopic fractions. However, isotopic fractionations were found for the front ( $\delta^{37}\text{Cl}$  -5.1‰) and tail ( $\delta^{37}\text{Cl}$  -1.8‰). Isolation of individual OCl by capillary gas chromatography enables accurate off-line analysis of the chlorine isotopes.

Combining Neutronic and Separation

An ecological issue is the production of  $^{36}\text{Cl}$  by neutron activation of  $^{35}\text{Cl}$ . The isotope  $^{36}\text{Cl}$  is a soluble (chloride, non-sorbing tracer) long live nuclide that makes it a first nuclide in the safety assessment of the repository. The build-up of  $^{36}\text{Cl}$  with burn-up for various  $^{35}\text{Cl}$  (activation product) enrichment what.

The neutron economical aspect is gained by better reactor criticality achieved through the use of enriched  $^{37}\text{Cl}$ . The criticality ( $k$ ) in zero power reactor conditions is much larger for enriched  $^{37}\text{Cl}$  than for the natural one. The reactor with 99%  $^{37}\text{Cl}$  would have a  $k$  of 1.04346 which improve the energy yield or would allow to reduce the required uranium enrichment and thus the fuel cost. This reactivity gain is evaluated for various  $^{37}\text{Cl}$  enrichment factors to estimate uranium enrichment gain achievable through  $^{37}\text{Cl}$  enrichment.

The reactivity gain (RG) increases with the salt  $^{37}\text{Cl}$  fraction, see Table 1. This increases consequently the neutron flux and the output power. An enrichment of 99% would be sufficient at beginning of life (BoL). Comparison of the  $^{129}\text{I}$  build up with  $^{36}\text{Cl}$  generation (both first nuclides) is very difficult because all iodine isotopes are discarded from the molten fuel by evaporation/boiling (together with the fission gases).

**Table 1.** Reactivity gain increases with  $^{37}\text{Cl}$  fraction in the salt.

$^{35}\text{Cl}$ (%)	$^{37}\text{Cl}$ (%)	RG (pcm)
75.8	24.2	0000
05.0	95.0	4118
01.0	99.0	4365
00.1	99.9	4421

The enrichment of  $^{37}\text{Cl}$  is needed and the use of efficient/performant isotopic separation technique is required. Table 2 reports a comparison of the separation factors revisited in this study.

**Table 2.** Comparison of separation factors for some techniques revisited in this study.

Separation	Conditions	$\alpha$	Ref
Centrifugation	$T$ : 300 K	1.0020	This work
Distillation	$T$ : 300 K	1.0060	Liebscher et al. (2006)
Chromatography	$T$ : 300 K	1.0003	Musashi et al. (2007)
Electrolysis	$T$ : 300 K Pt	1.0060	Johnston & Hutchison (1942)

Actually, the  $\alpha$  values are dissimilar from one extraction technique to another. They could be limited by isotopic exchange, kinetics and convections. Other issues reducing the separation factor are vibrations, artefacts, thermo-physical, or chemical effects (e.g.  $^{35}\text{Cl}_2$ ,  $^{35}\text{Cl}^{37}\text{Cl}$ ,  $^{37}\text{Cl}_2$ ) during separation. However other factors are to be taken in consideration the electrolytic data of 2 reported by Klemm require 1 week separation.

Production/enrichment of  $^{37}\text{Cl}$  can be proposed by gas centrifugation of  $^1\text{H}^{35/37}\text{Cl}$  and chemical separation or by elution of  $^{23}\text{Na}^{35/37}\text{Cl}$  in anion exchanger resin columns. The later requires however

extensive separation studies to reach higher separation factor. Alternatively the molten salt electrolysis is promising..

From an EROEI point of view gas centrifugation separation appears to be better than the chemical one because of a better separation factor. Recommendations need finally to be suggested combining the ecological and economical aspects of utilising  $^{37}\text{Cl}$  in the fast molten salt reactor.

## 5. Conclusion

The need of  $^{37}\text{Cl}$  in Molten Salt Fast Reactor for minimizing the ecological issues and for economic reasons is obvious.

The neutronic analysis has pointed out surprisingly large differences between codes which should lead to a two-fold strategy for improvement on the one hand differential cross section measurements as already pointed out by others, but on the other hand an integral reactor experiment, e.g. by using a pile oscillator, to provide a first reliable validation base for the code developers.

The specific ecological issue is the production of  $^{36}\text{Cl}$  by neutron activation of  $^{35}\text{Cl}$ . The isotope  $^{36}\text{Cl}$  is a soluble non-sorbing, in chloride form and long live nuclide that makes it a first nuclide in the safety assessment of the repository. The build-up of  $^{36}\text{Cl}$  with burnup has been explored for various fraction of  $^{37}\text{Cl}$  justifying the need of enrichment.

The neutron economical aspect is gained by better reactor criticality achieved through the use of enriched chloride in  $^{37}\text{Cl}$ . The criticality ( $k$ ) in zero power reactor conditions is much larger for enriched chloride than for the natural one. The reactor with 99%  $^{37}\text{Cl}$  would have a  $k$  of 1.04346 which improve the energy yield or would allow to reduce the required uranium enrichment and thus the fuel cost. This reactivity gain is evaluated for various  $^{37}\text{Cl}$  enrichment factors to estimate uranium enrichment gain achievable through  $^{37}\text{Cl}$  enrichment.

A centrifuge was one of the first device to separate  $^{37}\text{Cl}$  from  $^{35}\text{Cl}$ , as used by Jesse Beams of the University of Virginia in 1934. In 1940, American physicists thought that the centrifuge was the best possibility for large-scale enrichment. Over the last 80 years numerous techniques have been tested to achieve this separation. The present work revisits physical and chemical method.

Production/enrichment of  $^{37}\text{Cl}$  can be proposed by gas centrifugation of  $^1\text{H}^{35/37}\text{Cl}$  and chemical separation or by elution of  $^{23}\text{Na}^{35/37}\text{Cl}$  in liq – liq extraction or anion exchanger resin columns. The later requires however extensive separation protocol. The among the physical separation methods, gas centrifugation separation appears to be well adapted, from the while liq – liq extraction may promise better separation factor.

The combination of processes should be further explored. They reveal a large potential because the second process may quench the potential of mixing after preliminary separation using the separation scheme.

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