Development of a viable route for lithium-6 supply of DEMO and future fusion power plants

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ABSTRACT

In the European DEMO program, the design development of a demonstration power plant (DEMO) is currently in its pre-conceptual phase. In DEMO, breeding blankets will use large quantities of lithium, enriched in the isotope lithium-6 (^{6}Li), for breeding the tritium needed to feed the DT fusion reaction. Unfortunately, enriched lithium is commercially not available in the required quantities, which is threatening the success of future power plant applications of nuclear fusion. Even if the manufacturing of the breeding blankets is still two decades ahead of us, it is now mandatory to address the topic of lithium-6 supply and to make sure that a viable supply (and reprocessing) route is available when needed.

This paper presents an unbiased systems engineering approach assessing a number of available lithium isotope separation methods by defining requirements, rating them systematically and finally calculating a ranking number expressing the value of different methods. As a result, we suggest using a chemical exchange method based on a lithium amalgam system, but including some important improvements leading to a more efficient and 'clean' process (the ICOMAX process) in comparison with the formerly used COLEX process. Furthermore, by modelling activities and experiments in the KIT mercury laboratory (HgLab Karlsruhe), it is shown which work has to be done in the next years to make sure that the technical-scale process is available in time to supply DEMO and future fusion power plants by middle of the 21st century.

1. Introduction

In the fusion reaction considered for power reactors, the hydrogen isotopes deuterium and tritium are being used as fuel. Whereas deuterium is available on the market in sufficiently large quantities, tritium is not a primary fuel and has to be bred inside the reactor in so-called breeding blankets. These are actively cooled metallic 'boxes', installed on the walls of the reactor's vacuum vessel, and filled with lithium comprising materials (ceramics or eutectic fluids). Here, two nuclear reactions between the neutrons formed in the fusion reaction and lithium take place (Eqs. (1.1) and (1.2)) and form tritium, which is then extracted and used as fuel.

$$^6_3Li + ^1_0n \rightarrow ^3_1T + ^4_2He + 4.8 \text{ MeV} \tag{1.1}$$

$$^7_3Li + ^1_0n \rightarrow ^3_1T + ^4_2He + ^1_0n' - 2.5 \text{ MeV} \tag{1.2}$$

Unfortunately, using natural lithium (with an isotopic composition of about 7.6% lithium-6 and 92.4% lithium-7 [1]) as breeder material will not lead to a tritium breeding rate large enough for reactor self-sufficiency (when considering a blanket design that is technically feasible).

The only possible solution to overcome this problem is increasing the content of ^{6}Li to a level of some ten percent, strongly depending on the chosen breeding concept [2]. This works, as the cross-section of Reaction (1.1) is much larger than that of (1.2) at the fusion neutron energy spectrum [3], leading to a much more efficient tritium breeding.

The need for enriched ^{6}Li in large quantities (details see Chapter 2) asks for an isotope separation process that allows a minimum output of several tons of 'fusion grade' lithium (i.e. lithium with an isotopic composition that can directly be used in the blankets) per full power year. As far as we know, no facility is available world-wide that could satisfy this demand (discussed in Chapter 3), and it is also not straightforward to build such a plant. Hence, a suitable process has to be developed, which poses a special challenge for process engineers: Isotope separation is usually very energy demanding (what has to be optimized as far as possible) and complex, leading directly to large investments (what again has to be optimized as much as possible). A review of existing processes is done in Chapter 4 of this paper, resulting in a candidate process that can be used in a process plant.

In the last part of this paper, theoretical work/modelling (Chapter 5) and experimental work (Chapter 6) needed to develop an

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engineering design of a lithium isotope separation plant is presented and finally, in Chapter 7, a viable route towards the technical-scale production of 'fusion grade' lithium is proposed.

2. Requirements on lithium supply for a fusion reactor

The estimation of the required amount of lithium as well as its required enrichment level is a very difficult task to do. This requires a relatively detailed knowledge of the blanket and – in case of liquid breeders – the infrastructure system design. The latter includes all pipework, the cooling, cleaning, and tritium extraction systems.

The EU fusion roadmap concentrates on two main candidate blanket concepts, the water-cooled lithium lead and the helium-cooled pebble bed concept [4]. A good starting point for estimation is the work done for the DEMO liquid breeders. For the water cooled lithium lead (WCLL) blanket of a 2 GW$_{fus}$ (fusion power) device, a need of 844 m^3 (or 8′200 tons) of eutectic lithium-lead (PbLi), is assumed, comprising lithium enriched to 90% in ^{6}Li [5]. With a mass ratio of lithium in PbLi of 6.4·10^{-3}, this refers to an amount of 52 tons of pure ^{6}Li. This means that per GW$_{fus}$ 26 tons of 90% enriched PbLi are needed. These numbers are total inventories. The consumption of ^{6}Li depends on the tritium production rate (2 g ^{6}Li needed to produce 1 g tritium) and is small compared to the large total lithium inventory (112 kg ^{6}Li consumption per full power year and GW$_{fus}$).

In general, concepts based on liquid breeders can be assumed to have a larger inventory than the ones with a solid breeder [2]. Nevertheless, the amount of enriched lithium needed for any blanket concept is in the same order of magnitude, which means that some ten tons of 'fusion grade' lithium will be required. For solid breeders, 'fusion grade' refers to an enrichment level of 30–60%, for liquid breeders to up to 90% [2]. These values depend on blanket design parameters and neutronic calculations and are the result of a complex parametric optimization process [6] that shall not be discussed here.

3. History of lithium-6 production and current market situation

In the past, lithium isotope separation has initially been developed for thermonuclear bombs [7]. It was used during the cold war to generate ceramic lithium-6 deuteride (^{6}LiD) for the second stage of thermonuclear weapons [8]. In US, ^{6}Li enrichment took place in the Y-12 National Security Complex in Oak Ridge, TN. In the early 1950s, three processes have been tested in technical scale, OREX (organic exchange), ELEX (electrical exchange) and COLEX (column exchange) [8]. Not very many details of these processes are known, as all this work was classified or not documented. Nowadays, some background information on lithium enrichment activities in Oak Ridge have been declassified, giving us an insight in what has happened at that time. It is e.g. known that the COLEX process was found to be the most efficient process and enrichment has been done extensively in Y-12 between 1952–1963. A total amount of 442 tons of enriched lithium hydroxide has been produced [7], from which an unknown amount is still in the Department of Energy's stockpile in Y-12 in Oak Ridge and in K-25 in Portsmouth, Ohio [8]. Enrichment has been done using COLEX to a level of either 95.5%, 60% or 40%, leaving a residual of depleted lithium with a ^{6}Li content between 1–4%.

A huge problem of the COLEX (and also the ELEX) process was the environmental contamination. The exhaust air from the process plants (where mercury was handled in large, open columns and vessels) or the liquid waste from a nitric acid purification plant was for example released into the environment without further treatment. In total, approx. 330 tons of the more than 11'000 tons of used mercury have been lost in waste streams, by evaporation or spills [8]. Main reason for this large-scale contamination was the lack of knowledge on mercury chemistry (e.g. the formation of highly toxic organic compounds) and, due to the time pressure during that period, the accepted violation of environment protection measures. In addition, occupational health and safety was

not as strict as today, leading to a very relaxed handling of the toxic mercury, not using leak-tight equipment and well-monitored plants. A more historic background on lithium isotope separation, going back to the 1930s, is given in [9].

Similar detailed information about lithium enrichment in other countries is not existing or not accessible to the public. Nevertheless, it is believed that similar activities took place in UK, France, China, Israel [8], North Korea [10] and probably also in Pakistan, India and Russia.

Today, as far as we know, the very limited demand of ^{6}Li on the global market is supplied mainly by what has been produced in Oak Ridge in the 50 s and 60 s. Typical market prices (as of April 2019) for the small amounts sold on the free market are in the order of 53 k€/kg [11] (95% enriched). In 1982, the costs for enrichment based on the COLEX process was estimated to be around 1 k€/kg (90% enriched) [12]. The huge discrepancy between these two values results most likely from the missing supply route. If a large demand of ^{6}Li would come from the market, the prices would dramatically increase or, more likely and even worse, it will not be possible to satisfy the demand.

4. Isotope separation method selection

4.1. Methodology of the approach

As no plant for the supply of 'fusion grade' lithium in technical scale seems to be available, a method for lithium isotope separation must be identified that allows building a process plant to satisfy the future demand for this material. There are several methods for lithium isotope separation (see Chapter 4.3) that could theoretically be used, all with advantages and disadvantages. In this section we will explain how a suitable method has been selected and which work is still missing to mature a process based on this method towards a technical or industry scale plant that fulfils highest safety and environmental standards.

The evaluation of the isotope separation methods was done by a systems engineering approach according to a VDI guideline [13]. This approach ranks a certain list of criteria following the pairwise comparison method (Chapter 4.4) and, in a second step, calculates a ranking number that can be used for ranking different methods. This number W (varying from 0 to 100%) describes how good a method fulfils the criterion list generated by the pairwise comparison. As a result of the whole process, the ranking number W is available for each process considered, expressing the value of this process and allowing a direct comparison. The same approach has also been used in the development of the tritium, matter injection and vacuum systems for the European DEMO reactor [14,15].

4.2. Requirements on a technical-scale enrichment process

On a technical-scale enrichment process, there are a number of criteria that have to be considered in the pairwise comparison approach: Very important, the process has to be well scalable, as it is expected that upscaling towards large process plants will be required once fusion reactors for electricity generation are being built on global scale. As it is the case for all chemical processes, a low complexity and a robust and proven process is desirable. Furthermore, it should be as energy efficient as possible and the investment costs for a process plant should be low. Additionally, the production of toxic waste and the use of toxic and/or dangerous fluids should be avoided as far as possible.

In fusion reactors, the breeding material has to be reprocessed after the lifetime of the blankets to re-balance the ^{6}Li content to the desired value. (^{6}Li is preferably consumed in the breeding reaction, leading to a decrease of its enrichment level in ^{6}Li and, in consequence, a decrease in the breeding rate.) The enrichment process should thus be able to directly use the irradiated and tritiated materials to avoid a complex and expensive decontamination pre-treatment before going to the isotope re-balancing process. A summary of all requirements on an

Table 1
Criteria used for the pairwise comparison approach.

No.	Criterion used for pairwise comparison
1	Good scalability
2	Low complexity
3	Direct reprocessing of the blanket material possible
4	No production of toxic waste
5	No use of toxic fluids
6	Well proven / robust process
7	Good energy efficiency
8	Low investment required

Table 2
Result of the pairwise comparison approach.

	Good scalability	Low complexity	Direct reprocessing	No production of toxic waste	No use of toxic fluids	Well proven / robust process	Good energy efficiency	Low investment	SCORE	ORDER
Good scalability		1	0	1	2	1	0	0	5	5
Low complexity	1		0	0	1	0	0	0	2	6
Direct reprocessing	2	2		1	2	2	1	2	12	1
No production of toxic waste	1	2	1		2	2	1	0	9	4
No use of toxic fluids	0	2	0	0		0	0	0	2	6
Well proven / robust process	1	1	0	0	2		0	1	5	5
Good energy efficiency	2	2	1	1	2	2		1	11	2
Low investment	2	2	0	2	2	1	1		10	3

enrichment process is listed in Table 1.

4.3. Pairwise comparison

The pairwise comparison was done according to the following scheme: In a matrix structure (Table 2), each criterion presented in Table 1 is compared against all others in view of importance one by one (pairwise). If one of the criteria is more important than the other one, a 2 is filled in the matrix; if it is less important, a 0 is given; if both criteria are of equal importance, a 1 is given.

The result of the comparison approach is presented in Table 2. The order of importance for each criterion, determined by this method is shown in the very right column. A quantitative weighting value, required for the following calculation of a number (chapter 4.5) used for ranking different processes, is given in the neighbouring column (SCORE value).

For this approach, it is sufficient to fill the numbers on the right side of the diagonal line (black numbers). The numbers in grey are resulting due to the symmetry of the matrix and can be calculated by two minus the value reflected on the diagonal line.

4.4. Overview on considered enrichment methods

For lithium isotope separation, there are a number of processes known in literature. They can be used for the enrichment of ^{6}Li and most of them will be investigated on their applicability for fusion power plants in the next chapter. In general, all existing processes can be sorted into four major groups based on their working principle. These groups are: (1) Chemical exchange methods, (2) electrochemical exchange methods, (3) displacement chromatography methods and (4) laser-based methods.

Chemical exchange methods are two phase systems (e.g. liquid/solid or immiscible liquid/liquid), with lithium in both phases, but at different isotope ratios in thermodynamic equilibrium. The separation occurs due to small differences of the chemical properties (i.e. solubility) of the isotopes, which lead to a slight tendency for ^{6}Li to be

Table 3
Enrichment methods considered for this work.

No.	Criterion used for pairwise comparison
1	Lithium amalgam chemical exchange
2	Liquid ammonia chemical exchange
3	Cation complexing chemical exchange
4	Ion exchanger (organic)
5	Ion exchanger (inorganic)
6	Intercalation systems
7	Electrolysis (mercury cathode)
8	Electrolysis (other cathodes)
9	Electromigration
10	Electrophoresis
11	Displacement chromatography (inorganic resin)
12	Displacement chromatography (organic resin)
13	Separation by laser methods

favoured by one phase and ^{7}Li by the other. Chemical exchange systems that have been investigated in the past and that shall be mentioned here are the lithium amalgam system [16], cation complexing systems using mainly cyclic polyethers and cryptands [17], the liquid ammonia system [18], systems using organic or inorganic ion exchangers [9] and intercalation systems [19]. Electrochemical separation benefits from the effect of different mobility of lithium ions while traveling in a fluid or through a membrane. Methods mentioned here are electrolyses on mercury or other cathodes [20], electromigration [21] or electrophoreses [22]. Displacement chromatography is based on a chemical interaction between lithium solved in a mobile phase (liquid) and lithium adsorbed at a solid surface (organic or inorganic resin as stationary phase) [23]. Laser-based methods are generally based on the selective excitation of the desired isotope and its subsequent separation from the feed stream by electric or magnetic separation [24]. An overview of all methods considered in the systems engineering approach presented here is given in Table 3.

4.5. Ranking results for different processes

For decision making, it now has to be checked to what extent an enrichment method introduced in Table 3 meets the categories defined in Table 1 and weighted with the factor from the pairwise comparison as shown in Table 2. For this purpose, the resulting weighting value *g* (SCORE in Table 2) for each category has to be multiplied with a rating number *p*. This rating number can vary between 0 (dissatisfying), 1 (inadequate), 2 (sufficient), 3 (good) and 4 (very good, ideal). Finally, the ranking number *W* is calculated and expresses (in percent) how good the enrichment method fulfils the criterion on an ideal process. The maximum number of points an ideal process could reach is calculated by 4 (best rating) × 56 (sum of all weighting values) = 224. Hence, an ideal process reaching a *W* value of 100% would mean that 224 points are achieved.

The results for the chemical exchange systems are given in Table 4, the results for electrochemical separation, for displacement chromatography and for laser-based methods in Table 5.

4.6. Results of the selection process

The main result of the evaluation process can be easily extracted from Tables 4 and 5, respectively. The by far highest number is shown by the lithium amalgam chemical exchange process. Main reason for this is its good scalability and the possibility for reprocessing. It is a proven and robust process, not very complex and standard process plant equipment can be used (e.g. columns, pumps, electrolyses cells). Furthermore, the working fluid mercury is available in the required quantities – even if there are some regulatory specialities that have to be considered.

The working principle of the lithium amalgam chemical exchange

Table 4
Ranking results for chemical exchange systems.

	Weighting	Lithium amalgam chemical exchange		Liquid ammonia chemical exchange		Cation complexing chemical exchange		Ion exchanger (organic)		Ion exchanger (inorganic)		Intercalation systems	
		p	p x g	p	p x g	p	p x g	P	p x g	p	p x g	p	p x g
Good scalability	5	4	20	4	20	4	20	4	20	4	20	1	5
Low complexity	2	4	8	4	8	4	8	4	8	4	8	2	4
Direct reprocessing	12	4	48	4	48	0	0	0	0	0	0	4	48
No production of toxic waste	9	4	36	4	36	0	0	0	0	3	27	3	27
No use of toxic fluids	2	1	2	0	0	1	2	0	0	0	0	1	2
Well proven/robust process	5	4	20	0	0	2	10	1	5	1	5	1	5
Good energy efficiency	11	3	33	2	22	3	33	3	33	3	33	1	11
Low investment	10	3	30	3	30	3	30	2	20	2	20	1	10
Sum:	**56**		**197**		**164**		**103**		**86**		**113**		**112**
Ranking number W:			**87.9**		**73.2**		**46.0**		**38.4**		**50.4**		**50.0**

process is based on isotopic exchange between lithium amalgam and an aqueous lithium hydroxide solution, flowing in large counter current columns. The process comprises three steps: The amalgam formation (waste reflux) with electrolytic amalgam maker, a ^{6}Li enrichment section with the exchange columns and the amalgam decomposition (product reflux). A block diagram showing a schematic of the process including the main fluid streams is shown in Fig. 1. This process can be operated fully continuously. Some more information on the process can be found in literature [25].

In the past, a lithium amalgam chemical exchange process was used in US for large-scale lithium enrichment – the COLEX process – and caused significant environmental issues (see Chapter 3). Since that time, technology has been enhanced and environmental protection and monitoring as well as occupational health and safety have become an intrinsic element of each chemical plant development process. As consequence, if a process applying lithium amalgam as working fluid shall be applied today, no environmental issues would be expected (or the process would not be licensed at all).

As the result of the assessment is explicit, we are proposing to apply an improved lithium amalgam chemical exchange process, the so-called ICOMAX-process (short for Improved COlumn-based Mercury Amalgam eXchange), for the production of the breeder material needed for future fusion reactors. In this development, it is important to address all issues of the past and finally come up with a fully optimized process, fulfilling all requirements on a modern process plant.

4.7. Process development & maturation

The development of the ICOMAX process should be done in four stages: First, an assessment of the existing technology, that goes back to the 1940s and 50 s, has to be done to define weak points or missing information. Unfortunately, only few details and data of the historical process are available or accessible, as this process was classified in the past. Additionally, working procedure descriptions do not seem to exist and, hence, our knowledge in mercury and amalgam processing is very limited. For this reason we did not only do literature work, but also start experimental activities with the goal (i) to gain experience with this process and (ii) to produce the missing data for process engineering, like e.g. a scaling law for the exchange columns or operational parameters for the reflux sections. At KIT, a dedicated mercury laboratory, the HgLab Karlsruhe, has been set up for this purpose (see Chapter 6.2). The first development step should also include process modelling (see Chapter 5) and component design activities that run in parallel to the experimental activities. In the end, it is essential to know working fluid flow rates and component sizes. Without having access to this information, no process plant development or cost optimization can be done.

In a second step, technical-scale components have to be designed based on the information produced in the laboratory before and on the result of the modelling work. These components (like amalgam maker, enrichment columns and amalgam decomposer) have to be manufactured in technical scale and used to demonstrate scaling of the process equipment. As scaling from small (lab-)scale towards a process plant is not straightforward, this step is very important: small mistakes here will affect the overall capital investment and the running costs of a production plant significantly. In addition, important aspects for a clean and optimized process, such as mercury hold-up in the columns or the possibility of complete mercury removal (for maintenance, repairs or decommissioning), can only be demonstrated in this second step. For this second step, a test environment (or the first part of a pilot plant) is needed to allow design validation of technical-scale process equipment.

In step three, connection and combined operation of the equipment has to be demonstrated (because a large number of stages are required to achieve the desired degree of enrichment). Furthermore, process monitoring, diagnostics & control play now an important role. All this can only be done in a pilot plant that comprises all required equipment, but still has the flexibility to do some (smaller) changes in piping, instrumentation and control. Especially in the commissioning phase of this plant, lots of valuable information will be gained on process kinetics and plant operation. It is obvious that this third step means the construction of a dedicated facility and is an expensive, but necessary effort in the development of an ICOMAX process plant.

The fourth and final step is the demonstration of the reliability and robustness of the process while operating an enrichment facility at high production capacity (e.g. production of 1 ton lithium per year, enriched to 90% ^{6}Li). This can be done by an update of the pilot plant by the installation of additional columns or the construction of a dedicated plant. At the end of step four, a production plant should run at routine operation to produce the 'fusion grade' lithium required for the first set of DEMO breeding blankets.

A more detailed description of the estimated timescale for these steps is given in Chapter 7.

5. Modelling of a chemical exchange process

5.1. Approach

For every isotope separation process it is crucial to know the number of required separation stages and the flow rates of the working fluids. The latter is directly proportional to the size of the facility, its energy consumption and its inventories, whereas the number of separation stages needs to be known precisely to achieve the designed degree of ^{6}Li enrichment at a given throughput. Goal of the activity described here was the development of a tool that is capable to compute

Table 5
Ranking results for electrochemical separation, displacement chromatography and laser-based methods.

	Weighting	Electrolysis (mercury cathode)		Electrolysis (other cathodes)		Electromigration		Electrophoresis		Displacement chromatography (inorganic resin)		Displacement chromatography (organic resin)		Separation by laser methods	
		p	p × g	p	p × g	p	p × g	p	p × g	p	p × g	p	p × g	p	p × g
Good scalability	5	4	20	4	20	4	20	4	20	3	15	3	15	1	5
Low complexity	2	4	8	4	8	3	6	2	4	4	8	4	8	1	2
Direct reprocessing	12	4	48	3	36	2	24	3	36	3	36	0	0	4	48
No production of toxic waste	9	4	36	2	18	1	9	1	9	3	27	1	9	4	36
No use of toxic fluids	2	1	2	1	2	1	2	1	2	1	2	4	8	4	8
Well proven/robust process	5	4	20	1	5	4	20	1	5	2	10	2	10	2	10
Good energy efficiency	11	0	0	0	0	0	0	0	0	4	44	4	44	1	11
Low investment	10	3	30	2	20	2	20	1	10	3	30	3	30	0	0
Sum:	56	164		109		101		86		172		124		120	
Ranking number W:		73.2		48.7		45.1		38.4		76.8		55.4		53.6	

all information of interest for the ICOMAX process, giving us a feeling for the size and the design of the process equipment.

5.2. Single stage modelling

In a first step, modelling has been done for one separation stage. The single stage was modelled in steady state and with the following simplifications: (a) temperature and pressure are constant during the exchange process, (b) no impurities in the lithium, (c) large enough volume/contact time to achieve thermodynamic equilibrium, (d) the two liquid phases are immiscible, (e) lithium mass transfer only due to isotopic exchange, (f) no lithium solidifies or evaporates, no decomposition. Fig. 2 shows the model system with all relevant flows (explained in Table 6).

Entering into the system are the feed streams of lithium hydroxide solution and amalgam. Both contain a given amount of lithium with a specific isotopic abundancy. As the aqueous and mercury part of the flows are not partaking in the isotope exchange process, they can be omitted for modelling. Each stage is further characterized by a volume V, an operating temperature T and a pressure p.

Very important for modelling of the separation stage is the separation factor α, that has to be determined experimentally and that is a measure for the change of the isotopic composition while passing the stage. From literature it is known that the factor for the lithium hydroxide/amalgam system is in the order of 1.05 and shows a temperature dependency (lower temperature leads to a better separation, i.e. a larger α) [26]. A definition of the separation factor and the equations used to describe the single separation stage can be found in Table 7.

Applying assumptions (b) and (e), lead to a binary system with only the lithium fractions in both phases as non-constant quantities and the relations of Eqs. (5.4) and (5.5) can be used to further simplify the separation factor. This reduces the system to only 4 unknown variables with the fraction of lithium-6 in each flow. This set of equations was solved using the Aspen® Plus Custom Modeller. An analytical solution also exists and has been calculated and used to benchmark the numerical model. However, in preparation of the cascade modelling described in Chapter 5.3, also the single stage model was solved numerically.

The model can be used e.g. to calculate the ^{6}Li fraction at the outlet of the separation stage while using different separation factors α. The result of a parametric study with factors between 1–1.1 is presented in Fig. 3. At $\alpha = 1$, no isotope separation takes place and the mole fraction of ^{6}Li leaving the stage equals the natural isotopic abundancy of 7.6% in the feed flow. At technically realistic values between 1.04–1.06, the ^{6}Li fraction leaving the stage is at 7.76% what corresponds to an enrichment of ~ 2.2%.

5.3. Multi stage (cascade) modelling

For fusion applications, a lithium mole fraction of up to 90% is required. This asks for a cascaded arrangement of the separation stage modelled in Chapter 5.2. Therefore, the Aspen® model has been extended to model an arbitrary number of stages. A block diagram of the model is shown in Fig. 4. The nomenclature is identical with the naming introduced in Table 5. A reflux section has been introduced following the top stage S where the product stream can be withdrawn. This results in a so-called square cascade. The separation factor was assumed to be constant for every stage.

Every individual stage s in the cascade can be described as follows: Entering the stage is a lithium stream as part of the amalgam stream from the previous stage s-1 with the same composition as at the outlet of that stage $\tilde{x}_{s-1}$. The same stream is leaving the stage with a new composition $\tilde{x}_s$. Also entering the stage is a lithium stream as part of the lithium hydroxide solution from the next stage s+1 with the composition $\tilde{y}_{s+1}$. The same stream with the new composition $\tilde{y}_s$ is
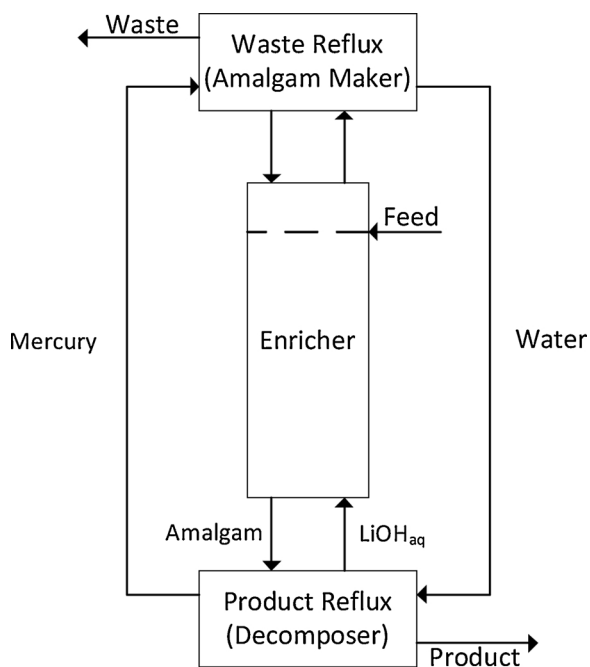
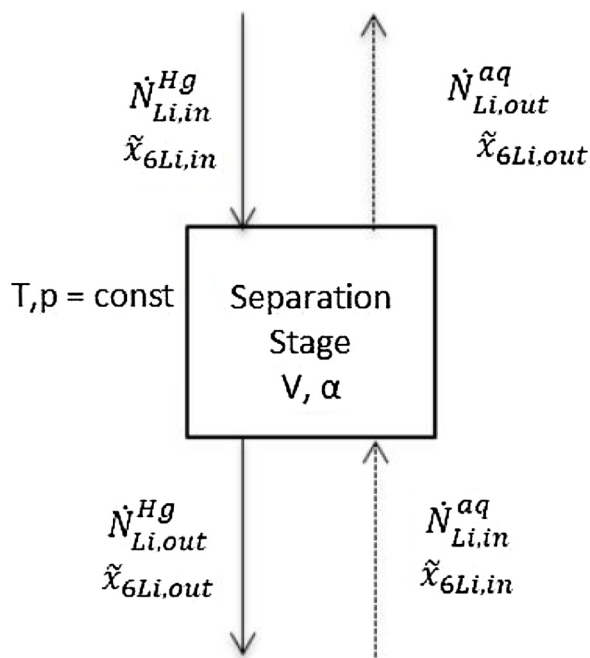Fig. 1. Schematic of the lithium amalgam chemical exchange process.

Fig. 2. Model of a single separation stage.

Table 6
Nomenclature of the flows through the single separation stage.

Variable	Description
$\dot{N}_{Li,in}^{Hg}$	Lithium flow in amalgam feed
$\dot{N}_{Li,in}^{aq}$	Lithium flow in LiOH solution feed
$\tilde{x}_{6Li,in}^{Hg}$	^{6}Li fraction of lithium in amalgam feed
$\tilde{x}_{7Li,in}^{Hg}$	^{7}Li fraction of lithium in amalgam feed
$\tilde{x}_{6Li,in}^{aq}$	^{6}Li fraction of lithium in LiOH solution feed
$\tilde{x}_{7Li,in}^{aq}$	^{7}Li fraction of lithium in LiOH solution feed
$\dot{N}_{Li,out}^{Hg}$	Lithium flow in amalgam return
$\dot{N}_{Li,out}^{aq}$	Lithium flow in LiOH solution return
$\tilde{x}_{6Li,out}^{Hg}$	^{6}Li fraction of lithium in amalgam return
$\tilde{x}_{7Li,out}^{Hg}$	^{7}Li fraction of lithium in amalgam return
$\tilde{x}_{6Li,out}^{aq}$	^{6}Li fraction of lithium in LiOH solution return
$\tilde{x}_{7Li,out}^{aq}$	^{7}Li fraction of lithium in LiOH solution return

Table 7
Equations used to describe a single separation stage.

| Eq.	Equation	Description
5.1	$\alpha = \dfrac{\tilde{x}_{6Li,out}^{Hg}}{\tilde{x}_{7Li,out}^{Hg}} \cdot \dfrac{\tilde{x}_{7Li,out}^{aq}}{\tilde{x}_{6Li,out}^{aq}} = \dfrac{\frac{\tilde{x}_{6Li,out}^{Hg}}{1-\tilde{x}_{6Li,out}^{Hg}}}{\frac{\tilde{x}_{6Li,out}^{aq}}{1-\tilde{x}_{6Li,out}^{aq}}}$	Definition of separation factor
5.2	$\dot{N}_{Li,in}^{Hg} = \dot{N}_{Li,out}^{Hg}$	Assumption of only isotopic exchange
5.3	$\dot{N}_{Li,in}^{aq} = \dot{N}_{Li,out}^{aq}$	
5.4	$1 = \tilde{x}_{6Li,out}^{Hg} + \tilde{x}_{7Li,out}^{Hg}$	Closing condition for binary system
5.5	$1 = \tilde{x}_{6Li,out}^{aq} + \tilde{x}_{7Li,out}^{aq}$	
5.6	$0 = (\tilde{x}_{6Li,in}^{Hg} - \tilde{x}_{6Li,out}^{Hg}) \cdot \dot{N}_{Li}^{Hg} + (\tilde{x}_{6Li,in}^{aq} - \tilde{x}_{6Li,out}^{aq}) \cdot \dot{N}_{Li}^{aq}$	Stationary molar balance for ^{6}Li
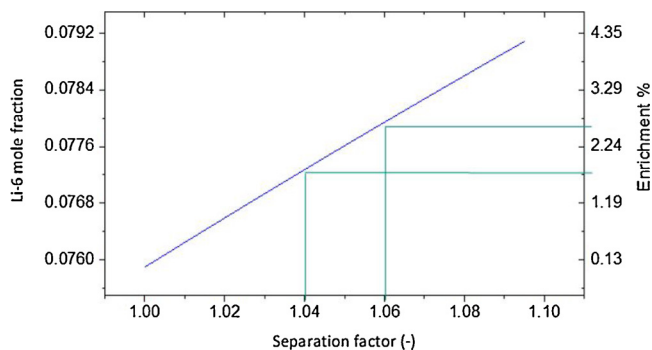
Fig. 3. Lithium-6 fraction in the lithium leaving the separation stage as function of the separation factor. (Equimolar feed assumed with natural isotopic abundancy of 7.6%.)

leaving the stage. To calculate the outlet compositions of each stage, the single stage model from Chapter 5.2 is used. A discrete stage in the cascade can therefore only be calculated completely, if the outlet composition $\tilde{y}_{s+1}$ of the following stage is known. This is a common problem in numerical methods (forward differences in finite difference methods). To solve the complete system, boundary conditions for the first and last stage are required. These can be derived from the feed stream and the reflux section. The feed stream (I_0, $\tilde{x}_0$) is assumed to be completely known in both flow rate and composition and is:

$$I_0 = \dot{N}_{Li,f} \tag{5.7}$$

$$\tilde{x}_{i,0} = \tilde{x}_{i,f} \tag{5.8}$$

The reflux section decomposes amalgam and forms lithium hydroxide solution according to:

$$\text{LiHg} + \text{H}_2\text{O} \rightarrow \text{Hg} + \text{LiOH}_{(aq)} + \tfrac{1}{2}\,\text{H}_2 \tag{5.9}$$
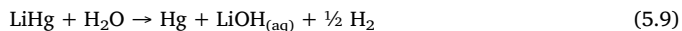
This reflux is assumed to work ideally and stationary. As for the single stage model, the streams of pure mercury and water have been omitted as they do not take part in the exchange process. Entering the decomposer is a flow of lithium (J_S) as part of the amalgam with the composition of the top stage S. As all lithium is assumed to be transferred between the two phases, the lithium composition $\tilde{x}$ and flow rate remains unchanged and a flow of lithium (J_R), now part of the aqueous solution, is leaving the decomposer. A part of the lithium hydroxide solution, determined by the reflux ratio R, can be withdrawn as product
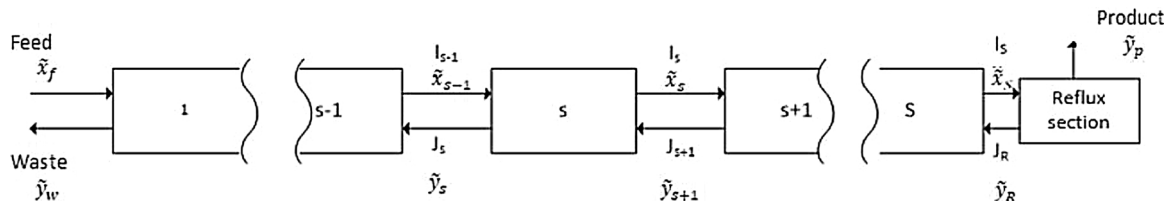
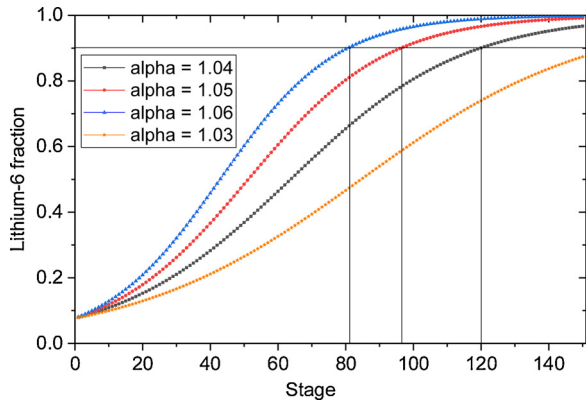**Fig. 4.** Model of a separation cascade with S stages.

Fig. 5. Model of a separation cascade with lithium-6 fraction at S stages.

(P). This is expressed by the following equations:

$$I_S = J_R - P \tag{5.10}$$

$$R = \frac{I_S}{J_R} \tag{5.11}$$

$$\tilde{x}_{6,S} = \tilde{x}_{6,R} = \tilde{x}_{6,P} \tag{5.12}$$

Similar to the single stage, the performance of the whole cascade is depending on the separation factor: Fig. 5 shows the ^{6}Li fraction in a cascade at total reflux (P = 0, $J_S = J_R$) with 150 stages and varying α, using a feed flow with lithium at natural isotopic abundancy (7.6%).

However, in a technical process, the total reflux assumption is unrealistic, since a certain amount has to be withdrawn as product of the enrichment process. In this case, the number of required stages will increase significantly, depending on the reflux ratio.

5.4. Summary of cascade modelling

The Aspen® model allows a variation of the reflux ratio and the separation factor and shows the impact on the number of required stages. This is a very important function: These two parameters are most important for process optimization, as they give a direct link between investment costs (i.e. size of plant) and operating costs (i.e. plant throughput).

It must be noted that the result of the modelling procedure gives only a number for the theoretical separation stages. This information alone does not help the process engineer to design a technical system: For doing so, another number that can only be determined experimentally has to be known, the HETP (Height Equivalent of a Theoretical Plate) value. Only by multiplying this number with the number of required theoretical stages S_{th}, coming from our model, the real height h_{column} of a separation column can be calculated:

$$h_{column} = HETP \cdot S_{th} \tag{5.13}$$

This value is not known to us and has to be determined in laboratory experiments.

6. Experimental studies in the KIT mercury lab

6.1. Approach

The determination of HETP values and separation factors can only be done experimentally and requires a working environment that allows the handling of mercury in quantities of the kg level. In addition, the optimization of process parameters, like the development of electrolyses cells with low over-potential and low mercury inventory (by adjusting the optimal contact time between Hg and the lithium hydroxide solution) requires such a laboratory. This was one of the main drivers for us to set up a mercury laboratory at KIT (HgLab Karlsruhe).

6.2. Description of the HgLab

For the work with mercury, different precautions must be taken: As mercury is highly toxic, skin and eye contact as well as inhalation of mercury vapour must be reliably avoided. The HgLab Karlsruhe has been designed to guarantee highest safety standards when handling mercury. The laboratory is located in a transportable 20″ container, equipped with a small locker room (4 m², Fig. 6) and a larger (11 m²) room for experiments (Fig. 7).

The container is heavily vented (change of air ventilation: > 80 h^{-1}) and air-conditioned to a temperature of less than 20 °C (vapour pressure of Hg at 20 °C = 0.0013 mbar). Additionally, the concentration

Fig. 6. The HgLab locker room.

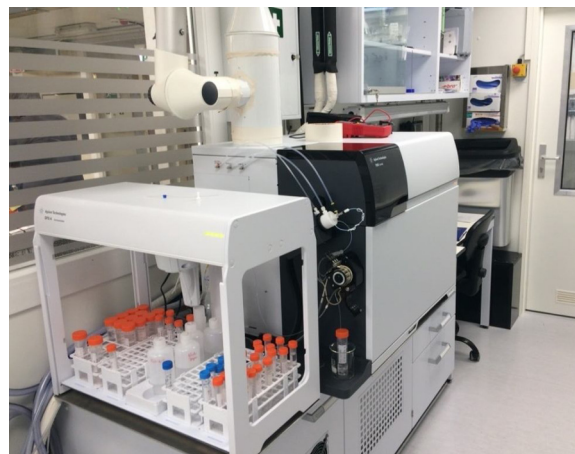**Fig. 7.** View into the HgLab experimental room.

of Hg in the laboratory air is checked continuously by an Atom Adsorption Spectrometer (AAS) system by Mercury Instruments (UT-3000) to assure that the MAK-value of $0.02\,mg/m^3$ [27] is not exceeded.

The experimental area of the lab is equipped with two hazardous material workstations, each providing 1.5 m of bench space for experiments and sample preparation, and two local exhaust points for our analytical device (Agilent 7900 ICP-MS, inductively coupled plasma – mass spectrometer). Beside this, three hazardous material sub-cabinets are available for storage of chemicals and waste which are continuously vented. A small desktop with workstation has also been installed to control the ICP-MS.

6.3. First experiments on lithium enrichment

For any work concerning lithium enrichment, it is of prime importance to have a method available to measure the lithium or impurity content in mercury and to determine the isotope ratio of the solved lithium. In this paper we will describe only the development of an analytical method and a first lithium enrichment experiment. More detailed work related to ICOMAX development is subject to future work.

For the quantitative measurement of lithium in mercury and the isotopic composition of the solved lithium, lithium amalgam has to be prepared first. Therefore, an electrolysis cell similar to the experiments of Palko et al. [28] and Fujie et al. [29] has been set up (Fig. 8).
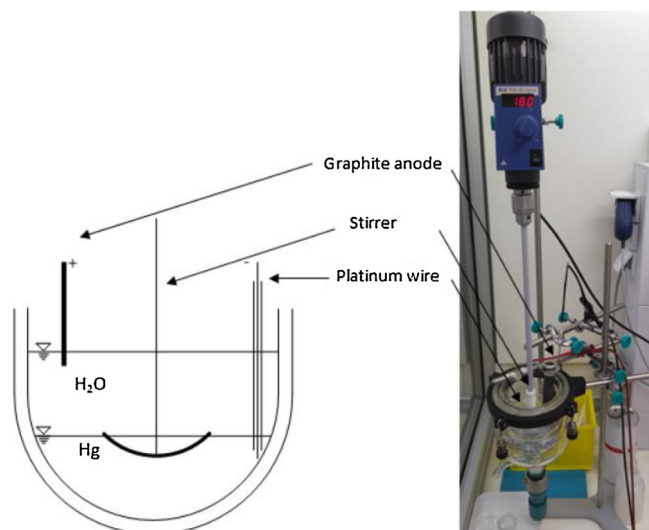

Fig. 8. Set-up for the electrolytic formation of lithium amalgam.

Fig. 9. The Agilent 7900 ICP-MS with autosampler (front).

The cell was housed in a jacketed reactor with a maximum volume of 500 ml and an inner diameter of 100 mm. The mercury cathode was supplied with current by a 0.1 mm diameter platinum wire fed through the aqueous phase inside a glass tube. A graphite anode with a diameter of 20 mm has been used. During the experiment, the mercury phase was stirred by a crescent shaped stirrer and the current was supplied by an laboratory power supply running at 7.5 V. Samples of both phases were taken at 0, 5, 10, 30 and 60 min. Therefore, the stirrer was turned off and samples were taken during a two minute time window.

For a reliable measurement of the samples by ICP-MS, calibration standards with known concentrations and known isotope ratios have to be prepared and measured. It has to be ensured that the samples measured are within the calibration range. Additionally, blank samples are required to compensate for background noise and lithium impurities introduced in the sample preparation process. To be able to measure several samples including calibration standards and blanks with a good repeatability and in short time, the ICP-MS was coupled with an autosampler as shown in Fig. 9.

The (quantitative) lithium standards were prepared out of a 10′000 ppm lithium solution (by Fischer Chemicals) by dilution to 1, 5 and 10 ppb using purified water with a maximum electrical conductivity of $0.055\,\mu S/cm$ and 69% nitric acid in analytical quality (VWR Normatom) with a certified lithium content of < 0.1 ppb. The same nitric acid was used for all standards and samples. To determine the recovery rate of the ICP-MS, a 200 ppb solution of scandium was used as internal standard. For lithium isotope ratio determination the reference material NIST RM 8545 (L-SVEC) was used which also serves as reference material for the natural isotopic abundance of lithium [1]. This lithium carbonate was dissolved in 100 ml of purified water and further diluted to concentrations of 1, 5 and 10 ppm. These dilutions were stabilized with 0.5 ml of concentrated nitric acid. For all calibration standards a blank sample of 0.1 ml HNO_3 in 9.9 ml purified water was used.

The mercury samples were prepared by weighing a portion of the original sample (< 20 mg) and dissolving it in 50 ml of 10% nitric acid using an ultrasonic bath for 1 h. For background samples either purified water of the same day or nitric acid from the same batch was used, respectively. Analytics on lithium isotope composition at the ICP-MS was done using a plasma power of 1500 W, 1000 sweeps of the elemental spectrum for 10 replicates per sample and an integration time of 3 s. Quantitative lithium samples were analysed with a plasma power of 1500 W, 3 replicates with 1000 sweeps per sample and an integration time of 0.3 s. Between all samples a blank sample comprising 5% HNO_3 washing solution was done. Obtained measurement results were the counts per second on the detector for each lithium isotope and, for quantitative measurements, the sample concentration calculated by the device out of the counts per second and the calibration standard at
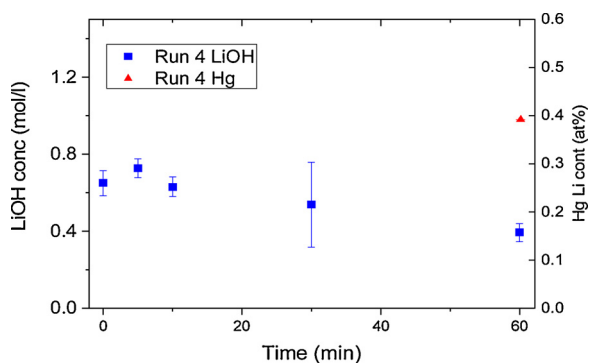
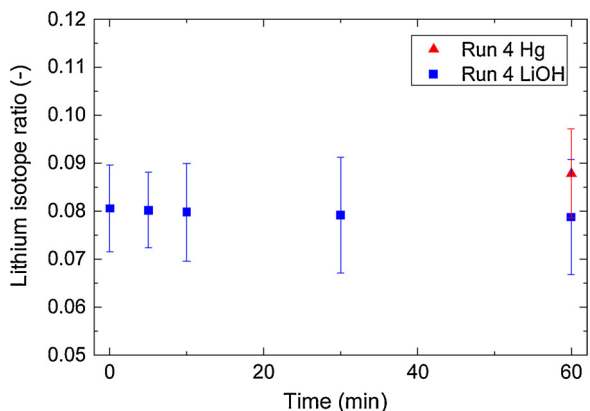**Fig. 10.** Lithium content in amalgam and aqueous phase.

Fig. 11. Lithium isotope ratios in amalgam and aqueous phase.

known concentration.

The results for one of the lithium amalgam preparation experiments are shown in Figs. 10 and 11, respectively. It can be seen that after 60 min, the concentration of lithium in the hydroxide decreases whereas the lithium content in Hg raises, indicating that amalgam was formed. This leads to a depletion of the aqueous lithium hydroxide solution. The isotopic composition after 60 min slightly decreases from the natural abundancy, whereas it increased in the amalgam phase, indicating that also enrichment took place during the electrolyses. From the amalgam, only one sample was taken after the experiment (after phase separation), as it is very difficult to avoid a systematic error due to contacting amalgam and lithium hydroxide during sampling.

It must be noted that the error bars are relatively large. For its calculation, the Guide to the expression of uncertainty in measurements (GUM) [30] was used to determine the expanded combined standard uncertainty in all measurements. The expanded uncertainty for a 95% confidence interval with k = 2 was used.

In summary, the first experiments in our new mercury lab showed that is very well suitable for experiments to support the development of the ICOMAX process. Despite several hours of open mercury handling, no unacceptably high mercury vapour in the room air could be detected and no spills inside and outside the laboratory took place. The development of analytical methods, essential for any future experiments, was successful and methods for quantitative determination of impurities and lithium in mercury, as well as for the measurement of lithium isotope compositions, are now available.

6.4. Outlook

As next step, two activities should be started in parallel: First, the determination of the HETP values (important for the design of the exchange columns) and second, the development and optimization of the amalgam maker/decomposer, which represent the waste and product

reflux sections.

HETP determination must be done for lab-scale exchange columns at different height, at different temperatures and using different packing materials. In preparation of the experiments, a thorough planning has to be done and suitable parameters to be varied must be determined. Goal of this work is the development of a reliable scaling law that allows the determination of heights, pressure drops and flow rate limitations for technical scale exchange columns.

The amalgam maker (waste reflux section) consumes a major portion of the energy needed in the enrichment process as lithium amalgam is produced, when a mercury cathode flows through a lithium hydroxide solution. The current needed for the cell scales directly with the amalgam production, but for the voltage, there is an ideal minimum of 2.8 V. This value can in reality not be achieved but with an optimized cell design, the over potential (i.e. the voltage difference between ideal and actual voltage value) is kept at a minimum and therewith also the wasted power, which is over potential times operation current. Not only the energy consumption can be optimized, but also the size of the cell and the mercury inventory, that has both to be minimized for economic reasons.

The amalgam decomposer (product reflux section) should also be as small as possible in order to minimize its mercury inventory. The contact time can be reduced dramatically, if an appropriate catalyst is being used. Unfortunately, also on the decomposer not many details are known from the old COLEX process and hence, a parametric study investigating the effectiveness of different catalysts has to be done in the laboratory.

7. Summary and proposal of a viable route for lithium-6 production

In this paper we have shown, how a viable route for lithium enrichment for future fusion reactors (DEMO and fusion power plants) could look like and what was the driver for our decision. Mainly due to the good scalability and its robustness, a chemical exchange process is strongly recommended. The formerly used lithium amalgam process (COLEX) has the advantage of a non-organic working fluid that does not decompose and produces toxic and/or tritiated waste. This makes the process applicable also for reprocessing of used (i.e. tritiated and irradiated) blanked material.

However, as experience from the past shows, this process must be optimized to avoid environmental issues, what can be done easily with nowadays technology. In addition, there is a lot of potential for optimization. Considering all this, the new process, called ICOMAX-process (Improved COlumn-based Mercury Amalgam eXchange) is being proposed. For its development and maturation, the HgLab Karlsruhe has been set up at KIT and is now available for the development of the most important units of the ICOMAX process (i.e. exchange columns and reflux sections). The commissioning of the laboratory has been presented in this paper as well as its capabilities and the planned next steps.

Based on the assumption that a first demonstration power plant (DEMO) shall be operational in Europe in the 2050s, a time plan for lithium enrichment can be elaborated by a simple backwards-calculation. This schedule, starting now and reaching until mid of the century is shown in Fig. 12.

Considering that DEMO shall be operational in the 2050s, manufacturing of the blankets must be started in the mid-2040s. Already for this step of DEMO construction, several tons of enriched lithium will be needed. Even if the total amount and the required enrichment level depends strongly on the breeding concept and can only be estimated today, a fully operational production plant is needed in the late-2030s (result of development step 4 as explained in Chapter 4.7). Previously, pilot plant update and tuning is needed, that will take approximately half a decade, meaning a start of this activity by the early 2030s. Precursor of this activity is the integrated testing of the whole ICOMAX
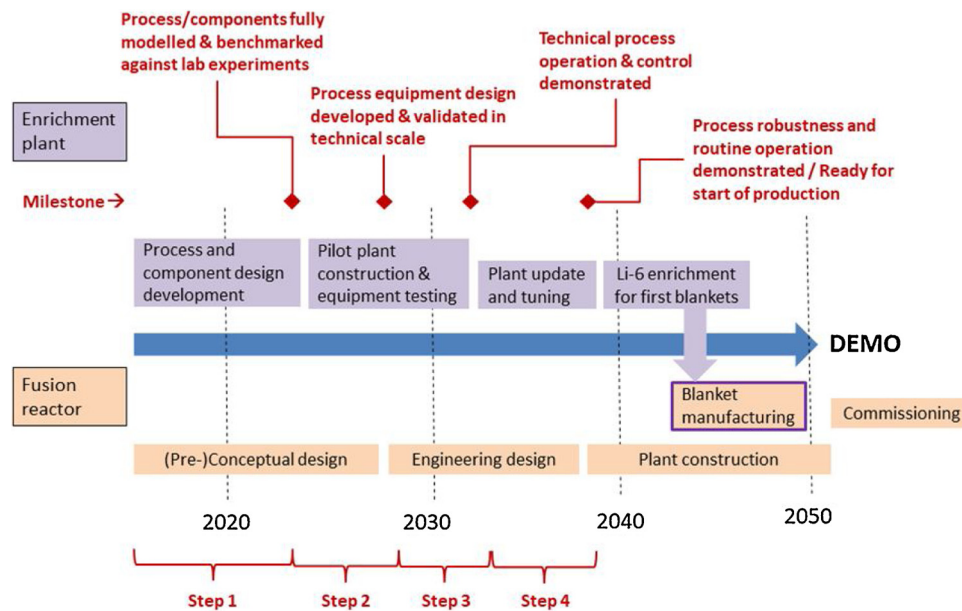
Fig. 12. Suggested schedule for a lithium enrichment route for DEMO.

process (step 3) that will take some years and, again before, the set up and commissioning of a pilot plant facility and testing of technical-scale components (step 2). Assuming that facility design and construction takes some years, the design of the process equipment and the result of the process development must be available by mid-2020 the latest. To keep this schedule, it is very important to start the time-consuming experimental activities, which is the design development for the exchange columns and for the reflux sections (step 1) now. The work has already been prepared by the development of the required experimental capabilities.

Declaration of Competing Interest

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