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Abstract
<p>Highly pure water is required for the treatment of silicon wafers during solar cell manufacturing. The main amount of it is consumed during the rinsing of wafers after etching and cleaning steps. Most commonly, this water goes down the drain without much further treatment or is fed into the waste water treatment system together with the more concentrated bleed from the processing bathes.</p> <p>In order to reduce the ecological footprint of solar cell manufacturing, we suggest to collect the rinsing water and re-introduce it to the water purification system. The work is based on the Ecosolar approach for the manufacturing of mc-solar cells based on an optimized process that consumes much less chemicals compared to a typical industrial process. The properties of the collected rinsing water are calculated based on measurements at ISC Konstanz' pilot line to show that reuse is possible. Without extra treatment, we show that 96 – 97% of the employed water can be recycled with neutralization as only treatment.</p>

Public introduction¹
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¹ All deliverables which are not public will contain an introduction that will be made public through the project WEBSITE

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1 INTRODUCTION

Solar cell manufacturing heavily relies on the use of ultrapure deionized (DI) water. On the one hand it is used for the make-up of wet chemical etching and cleaning baths, and on the other hand it is used for rinsing off the chemicals after etching and cleaning. The latter use makes up the largest part of the overall DI consumption. In order to remove remains of cleaning and etching bath components, and to prevent carry over into subsequent process baths, the wafers are commonly excessively rinsed.

The overall consumption of DI-water accumulates to several thousands of cubic meters per year. For example, every single solar cell produced requires about 5 L of DI water in the SoliTek solar cell production (see midterm LCA of this project). With tens of millions of cells produced every year one can easily see that the DI water consumption is quite large. In terms of total water consumption it is in a similar range as cooling water, which is required in many machines (see midterm LCA of this project). Whereas cooling water can easily be reused after cooling down in heat exchangers, the rinsing water is commonly not recycled. After it has been prepared in a costly multiple step purification system (compare Table 1), and an only one time use (or two or three time use in cascade systems), it is commonly either directly dumped or added to the concentrated drain (bleed from process baths) for waste water treatment (i.e. neutralization and fluoride precipitation), despite the fact that at least at some points it might still be significantly cleaner than the incoming city water.

Table 1: Price for DI-purification (3 step system, softening, reverse osmosis and ion exchange) calculated for system in use at ISC Konstanz

DI-price in Euros/m ³	
DI-prices without city water	11,544
city water costs	3,62
total	15,164

The concept of “zero discharge” in terms of water usage in solar cell manufacturing has been suggested before [1], however, concrete calculations have not been shown. The two key issues indicated in [1] are F^- and NO_3^- content of the waste water. In order to mitigate these issues, we suggest to change the process to minimal HF and HNO_3 consumption – in turn the waste water treatment may be vastly simplified (and become much more cost effective).

In the following, we firstly present a more eco-friendly solar cell process that relies on less etching and cleaning steps, alkaline instead of acidic etching, and lower acid concentrations. Then experimental data on the carry-over from process baths to rinses combined with flow measurements are used for calculation of rinsing water quality in terms of pH, conductivity and fluoride concentration (F^-). The thus obtained data is used to estimate the quantity of the used water and how much of it may be reintroduced into the water purification system.

2 APPROACH

2.1 Water purification

Commonly, a three step purification system is employed for the preparation of ultrapure DI water from city water. One example for a sequence of ion exchange trains to obtain first **purified water** from city water, second **pure water** and last **ultrapure** water from city water is sketched in Figure 1 (see also <https://www.lenntech.com/applications/process/demineralised/deionised-demineralised-water.htm>) . The scheme and the values are from a solar cell production line, no longer in operation.

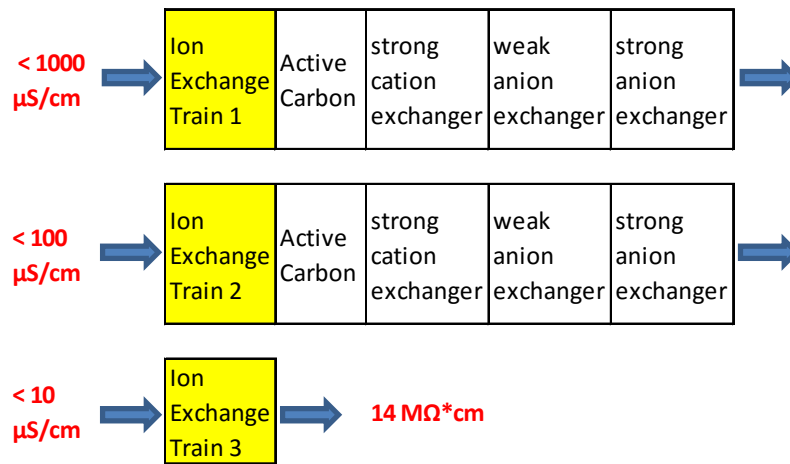


Figure 1: Example for a three step water purification system (values and drawing based on an actual system that was in operation in a solar cell manufacturing line).

Alternatively, as employed at SoliTek and ISC Konstanz, **water softening**, in which Ca^{2+} and Mg^{2+} ions are removed and exchanged for Na^{+} can be followed by **reverse osmosis** purification to obtain pure water. Last, similar to the method above, a last **mixed-bed ion exchanger** may be used to produce ultrapure water. It is assumed that the specs of the incoming and outgoing water of each of the three steps is not very much different in this case.

2.2 Waste water treatment

All acidic or alkaline solutions need to be neutralized. High concentration chemicals containing waste water commonly needs to be treated additionally before it can be dumped. Concentrated fluoride containing solutions are commonly treated on site. F^{-} is removed by precipitation as CaF_2 by adding $\text{Ca}(\text{OH})_2$ (lime water) or CaCl_2 . CaF_2 usually finds no further application than landfill, HF is usually not recovered. After neutralization the remaining water is dumped.

More problematic are high HNO_3 concentrations. Nitrate containing waste water must not be dumped in most countries to avoid contamination of waterbodies and drinking water. So concentrated HNO_3 containing solutions have to be collected and sent away for treatment. In principle, HNO_3 may be recovered by vacuum distillation, a costly energy consuming process. As a consequence, the Ecosolar process completely bans the use of HNO_3 . In addition to that low concentrations of other chemicals, in particular HF, are used so that apart from the rinsing water also the water from the process baths may be reused more easily.

2.3 Ecosolar process

The main goal of the Ecosolar project is to reduce harmful consumables wherever possible. For this purpose, experiments were run to reduce required chemical treatment steps to a minimum and/or to exchange harmful substances with less harmful substances, if possible without compromising the outcome efficiency. One of the most harmful and dangerous substances that was meant to be reduced was hydrofluoric acid (HF). As already elaborated in D3.1 and D3.2 the toxicity of this substance is extremely high.

The first measure is to replace the acidic texturing process, which, in addition to HF, produces large amount of nitrate (NO₃⁻) in the waste water and nitrous gases (NO_x) in the exhaust air, by alkaline processing. The ingredients of the acidic texturing baths are usually HF, HNO₃ and CH₃COOH. The advantage of the alkaline processing is that only hydrogen is generated during the etching and lower concentrations may be used. Instead of cooling as for the acidic baths, the alkaline cleaning baths need heating in order to reach sufficiently high etching rates. Due to slower etching in diluted KOH, treatment times need to be in the range of 3-5 min, whereas for the acidic process 30 sec to 1 min treatment time is sufficient.

The main reason against the use of alkaline texturing solutions in mc wafer fabrication is the anisotropy of the alkaline texturing process. The textured Cz surfaces (with [100] crystal orientation) form nice and regular random pyramids. As multicrystalline silicon surface have no defined crystal orientation, the surface structure of each grain after texturing is different. One can observe pyramids, polished grains and tilted pyramids of any kind. Hence, alkaline textured mc wafers have a higher reflectance compared to Cz wafers and also as acidic textured mc wafers. As shown in the literature [2,3], solar cell efficiency with alkaline texturing process is below the efficiency of traditional acidic textured wafers, but the module power performance is similar. Considering the current trend towards diamond wire sawing, which leaves a surface that yields a significantly higher reflection after texturing than conventional slurry sawing does, this cell based loss is expected to further decrease. An experiment confirming this is planned and will be performed before the end of the Ecosolar project.

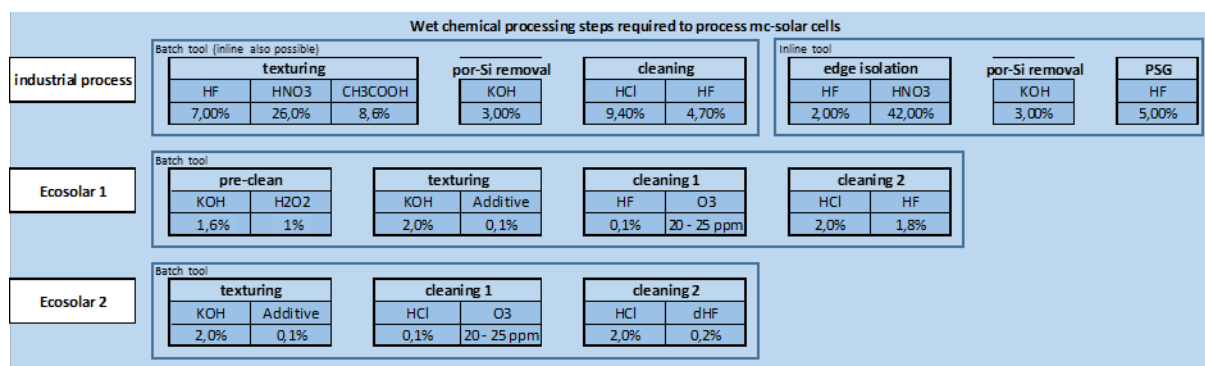


Figure 2: Wet chemical treatment steps required for the manufacturing of solar cells. The industrial process is based on the SoliTek factory. The Ecosolar 1 scenario is based on the standard process for Cz-wafers at ISC Konstanz (with laser edge isolation and omitting the PSG etching). The Ecosolar 2 approach is a further adjustment towards minimal chemicals consumption based on experimental data).

The second significant change is to replace the acidic single side etching used for edge isolation. This may be replaced by a conventional laser process, which is applying a laser trench on the front side of the solar cells to avoid shunts. This, however, yields in a loss in

current due to a decrease in active area. We suggest to employ a new Ecosolar laser process instead that actually applies the laser trench on the edge of the wafer (yet to be tested). A drawing of the prototype is displayed in Figure 3.

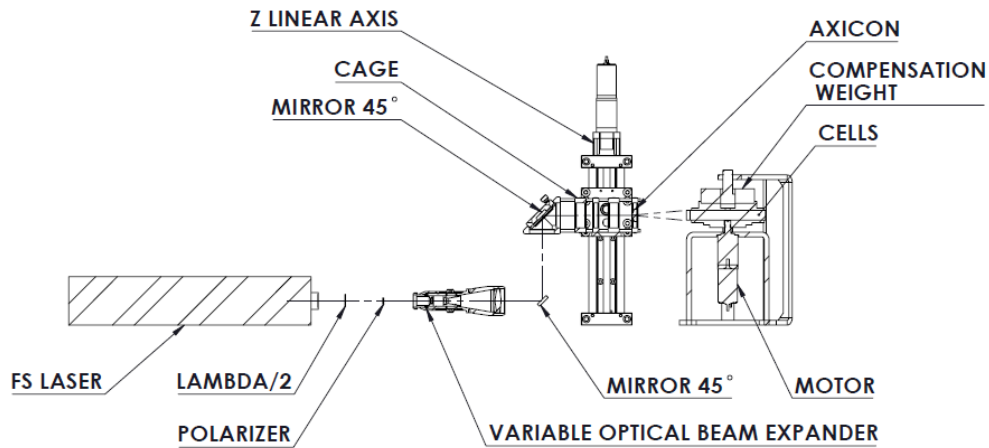


Figure 3: Ecosolar laser setup for applying the laser trench on the actual edge of the wafer.

The third change in process is using a low pressure POCl_3 diffusion with the newly developed recipe (see D3.2) that enables us to use the resulting phosphorus silicate glass (PSG) layer as passivation layer. The HF based PSG removal can be left out.

In order to get sufficiently clean surfaces after alkaline texturing, oxidative cleaning is required [4]. This is realized by injection ozone to a much diluted acidic solution as suggested in [4]. The main difference between the scenario Ecosolar 1 and 2 (compare Figure 2) is that the pre-clean is left out, which has been shown to have hardly any impact on the efficiency. For Cz wafers an additional saw damage etch (in concentrated KOH) showed the main impact on texturing quality. As the pyramid quality is expected to be of minor importance on mc wafers (pyramids will be tilted or non-existent anyway), we assume that this step can well be left out. However, as KOH pre-etching does not require separate rinsing, the impact on the overall rinse water consumption may be neglected. Moreover, based on recent results, HF in the ozone fed bath can be replaced by HCl, and the HF-concentration in the oxide strip (cleaning 2) can be reduced by a factor of about 10, as shown in Figure 4. These results were obtained on lifetime samples (p-type Cz-wafers). The wafers were textured, cleaned, POCl_3 diffused and passivated on both sides. The implied V_{oc} , as derived from lifetime measurements, is a good indicator for cell performance.

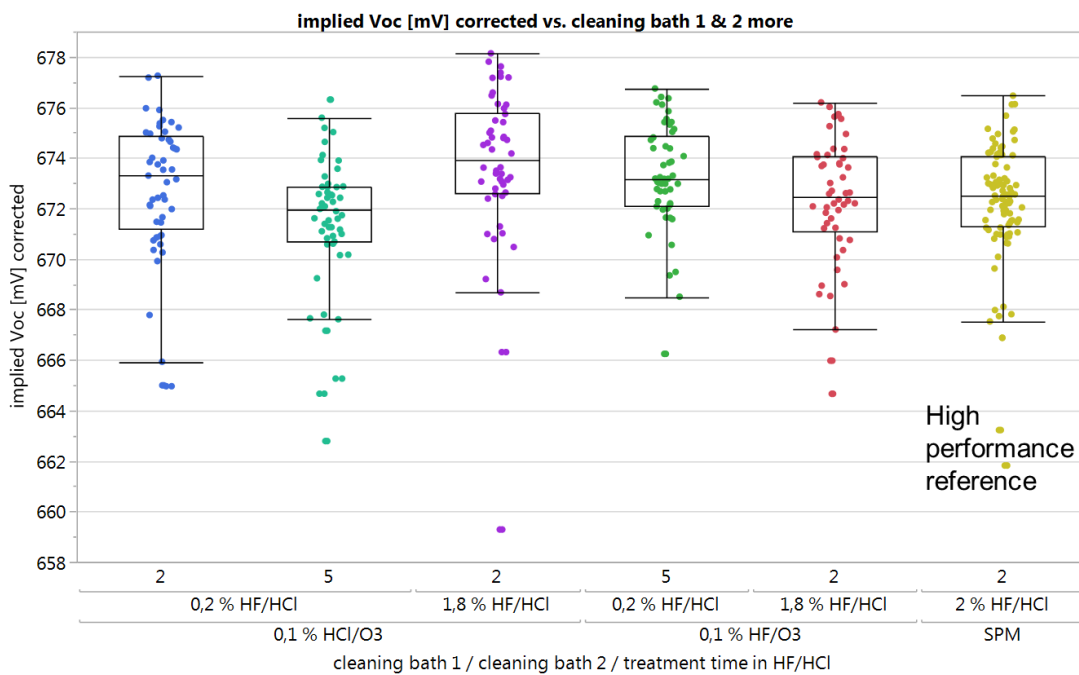


Figure 4: Implied V_{oc} values of symmetrical lifetime samples (alkaline texturing, P-diffusion, SiNx deposition on both sides). Corrected for diffusion boat position. Excellent cleaning results obtained by low-HF cleaning sequence (blue symbols).

2.4 Experimental design

The Ecosolar process approaches (1 and 2) for manufacturing of mc solar cells are used as the two scenarios to be considered and compared with industrial data. The rinsing water consumption and the resulting water properties are calculated, the waters are hypothetically mixed and treated. Based on the final outcome it can then be decided if it may be reused and in which purification step. The calculations are based on experiments in the ISC Konstanz pilot line. The key factor for those calculations are the carry-over volumes from the processing baths, as they make up for the largest amount impurities in the rinsing water.

3 EXPERIMENT AND RESULTS

3.1 Setup of rinsing experiments

PTFE-coated cassettes containing 50 wafers were used in a semi-automatized wetbench (fabricated by RENA). The volume of the overflow rinses was determined to be 40 L (by measuring the water flow and time it took to fill the bathes). A scheme of the overflow rinse can be found in Figure 5 **Fehler! Verweisquelle konnte nicht gefunden werden..**

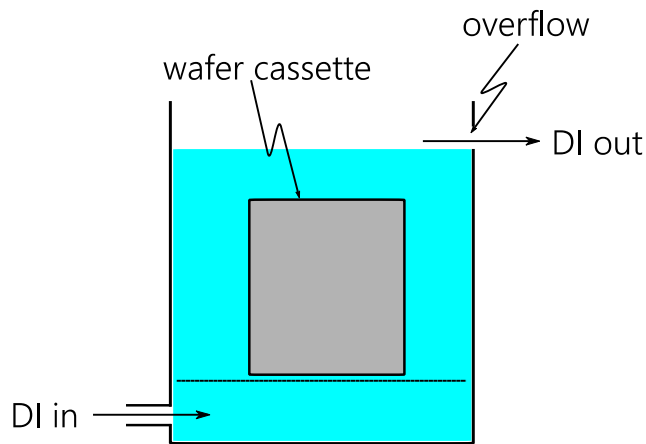


Figure 5: Sketch of an overflow rinse.

Wafers were treated in the respective etching or cleaning baths before rinsing. Rinsing after the pre-clean, after texturing and after cleaning 2 were investigated. As the concentration of the cleaning bath 1 is very low, no rinsing between the two steps is necessary. Rinsing consisted of a first longer rinsing step (1:00 – 5:00 min) followed by a quick step of 0:15 minutes. The water in-flow was determined using built in flow meters and adjusted to 0.19 L/sec for all rinses.

The concentrations of the relevant process baths are summarized in Figure 6. As the concentration of the cleaning bath 1 is very low, no rinsing between the two steps is necessary.

Ecosolar 1	pre-clean		texturing		cleaning 1		cleaning 2	
	KOH	H2O2	KOH	Additive	HF	O3	HCl	HF
	1,6%	1%	2,0%	0,1%	0,1%	20 - 25 ppm	2,0%	1,8%

Figure 6: Concentrations of the investigated cleaning baths.

The detailed process sequence is shown in Table 2. The longer rinsing times after the alkaline processing steps are due to larger carry-over from the process baths (as elaborated in the following chapter).

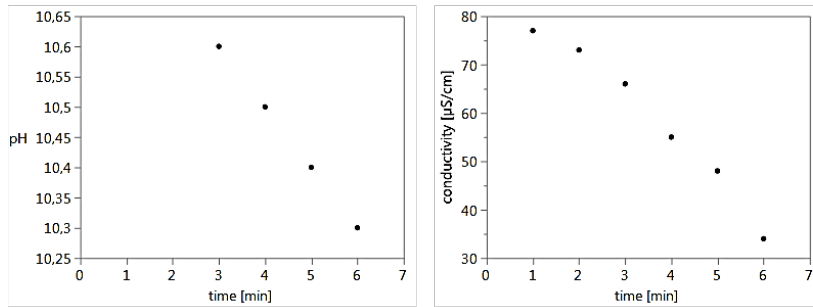
Table 2: Sequence of process steps including processing times and rinsing volumes at ISC Konstanz.

	process step	time [min]
0	Start	0
1	Rinse	00:15
2	KOH/H ₂ O ₂	05:00
3	Rinse	05:00
4	Rinse	00:15
5	alkaline Tex	13:00
6	Rinse	05:00
7	Rinse	00:15
8	HF/O ₃	10:00
11	HF/HCl	02:00
12	Rinse	01:00
13	Rinse	00:15

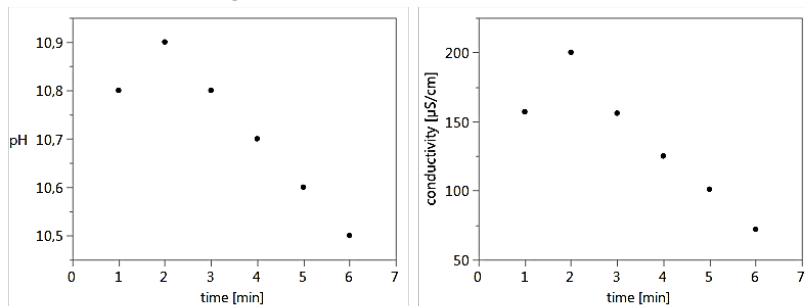
3.2 Determination of carry over volumes

First of all, conductivity, pH and fluoride concentrations were measured using a handheld measurement device (Mettler Toledo Multipurpose Handheld) allowing for the use of different electrodes (InLab, PerfectION). The value over time plots for the three relevant rinsing steps are shown in Figure 7.

After KOH/H2O2



After texturing



After HF/HCl

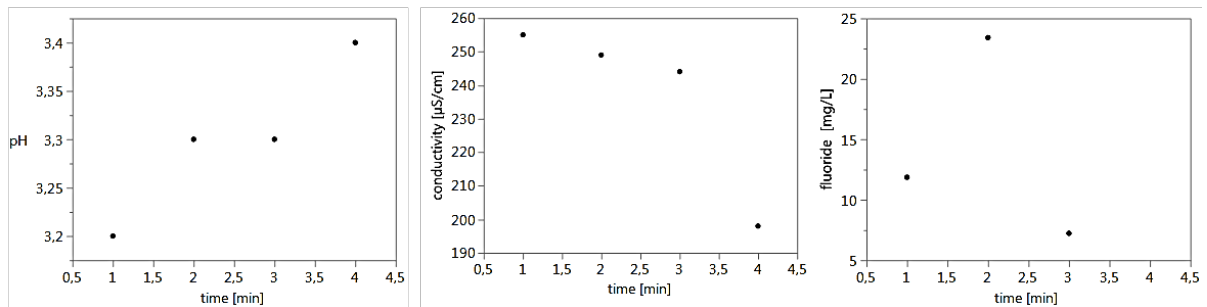


Figure 7: Measurements of rinsing processes using handheld pH electrode, conductivity and fluoride measuring equipment.

The maximum pH values (usually obtained after one or two minutes rinsing, see Figure 7) were used to calculate the carry-over from the carrier and wafers, which is the amount of process bath solution that is sticking at wafers and carrier. This time was assumed to be enough for proper mixing and the change in volume in that time frame was considered small enough for a good estimation. The measurements and calculation results of the carry-over volumes per carrier and per wafer are summarized in Table 3.

Table 3: Carry over volumes calculated from pH-measurements.

rinsing after	max /min value pH	wafer surface state after process	volume rinse V ₂ [L]	process chemicals	stronger acid/base c ₁ (1) [mol/L]	weaker acid/base c ₁ (2) [mol/L]	ratio c ₁ (2)/c ₁ (1) for mixture acid concentration calculation	conc c _r [mol/L] from max pH (1)	carry over total volume [L]	carry over V _w [mL] per wafer
KOH/H2O2	10,6	hydrophilic	40	KOH (1)/H2O2 (2)	0,293	0,296		3,98E-04	0,054	1,087
texture	10,9	hydrophil	40	KOH (1)/additive (2)	0,362			7,94E-04	0,088	1,755
HF/ozone	4,3	hydrophil	40	HF (1)/O3 (2)	0,051			5,39E-05	0,042	0,846
HF/HCl	3,2	hydrophobic	40	HCl (1)/HF (2)	0,556	0,912	0,61	5,63E-04	0,025	0,494

Obviously, the carry-over depends on the surface – whether it is hydrophilic or hydrophobic – but it also depends on the process bath solution.

3.3 Calculation of rinsing water volumes and properties

Using the respective carry over volumes and immersion times in the respective rinses the total water consumption was calculated. In order to reach sufficiently low conductivity values the rinsing in the rinses directly after the processing baths is continued for several minutes after the carrier has been removed, overall volumes including this post rinsing were considered. The overflow from the two rinses from each process baths were “collected” in virtual buffer tanks. The properties (pH, conductivity and F⁻, Cl⁻ and K⁺ concentrations if applicable) were calculated using the Aquion Pro 6.5.1 Software (<http://www.aqion.de/>). The water from each chemical process step was then collected and finally mixed and neutralized.

3.3.1 Rinsing water Ecosolar 1

Table 1 shows the calculated buffer tanks after each of the rinsing steps, the values are based on the measurements from Figure 6. A very short pre rinse is used before the wafers were immersed into the first process baths. The buffer tanks after the processing baths are fed by two rinsing baths. First, the immediately following rinse after each step, and second, a short dip in a second rinsing bath. The buffer tanks are added to the process sequence in Table 4.

Table 4: Ecosolar 1 sequence of process steps including processing times and rinsing volumes at ISC Konstanz.

	process step	Concentrations employed	time [min]	water consumption [L]	water consumption with post rinsing times [L]	Virtual buffer tanks
0	Start		0			
1	Rinse		00:15	2,9	2,9	Pre-rinse (0)
2	KOH/H2O2	1,6%/1%	05:00			
3	Rinse		05:00	57,1	97,0	Pre-clean (1)
4	Rinse		00:15	2,9	2,9	
5	alkaline Tex (KOH/add)	2%/0,1%	13:00			
6	Rinse		05:00	57,1	97,0	texturing (2)
7	Rinse		00:15	2,9	2,9	
8	HF/O3	0,03%/20ppm	10:00			
11	HF/HCl	1,8%/2%	02:00			
12	Rinse		01:00	11,4	51,4	Cleaning P-diff (3)
13	Rinse		00:15	2,9	2,9	

The resulting mixture concentrations as calculated are found in Table 5. The typical industrial batch size is 100 wafers per carrier. Also, the volume typical roughly scales with number of wafer per batch (40 L for 50 wafers ~80 L 100 wafers, ~160 L for 200 wafers). So we can safely assume that when doubling the wafers per batch, the bath volume also roughly doubles. Scaling to 100 wafers per batch has the advantage that the comparison with data as provided by SoliTek is simplified.

Table 5: Mixture concentrations and volumes for Ecosolar 1 scenario.

	buffer tank pre rinse	buffer tank precleaning (1)	buffer tank texture (2)	buffer tank cleaning P-diff (3)	mixing tank total	mixing tank neutralized
	per 50 wafers	per 50 wafers	per 50 wafers	per 50 wafers	per 100 wafers	per 100 wafers
pH value	5,62	10,20	10,50	3,32	9,70	7,00
conductivity [$\mu\text{S}/\text{cm}$]	0,93	45,40	87,70	203,00	33,00	26,80
fluoride [mg/L]	-	-	-	7,87	1,66	1,66
chloride [mg/L]	-	-	-	8,95	1,89	3,73
potassium [mg/L]	-	6,61	12,80	0,00	7,55	7,55
volume [L]	2,85	99,86	100,00	54,29	513,99	513,99

The overall consumption of ultrapure DI water is 514 L per batch or 5.14 L per solar cell. The pH of the resulting mixture is with 9.7 slightly alkaline, thus neutralization is applied. The last column shows the solution properties after neutralization with 33% HCl. When looking at the properties of the overall mixture one can immediately see, that the conductivity is still well below 100 $\mu\text{S}/\text{cm}$ and thus the drained rinsing water still qualifies as purified water and can be reinjected into the second step of a three step purification system as displayed in Figure 1. Fluoride and other ion concentrations are found on the ppm and sub ppm level, concentrations that can be easily handled by ion exchange columns or reverse osmosis systems.

3.3.2 Rinsing water Ecosolar 2

A further reduction in process water volume is found when the pre-clean step is left out. The fluoride concentration is reduced, when the HF/O₃ is replaced by HCl/O₃ and the HF concentration in the HF/HCl bath is reduced by a factor of ~10. The resulting Ecosolar 2 process sequence can be found in Table 6.

Table 6: Ecosolar 2 sequence of process steps including processing times and rinsing volumes.

	process step	Concentrations employed	time [min]	water consumption during process [L]	water consumption with post rinsing times [L]	Virtual buffer tanks
0	Start		0			
1	Rinse		00:15	2,9	2,9	Pre-rinse (1)
2	alkaline Tex (KOH/add)	2%/0,1%	13:00			
3	Rinse		05:00	57,1	97,0	texturing (2)
4	Rinse		00:15	2,9	2,9	
5	HCl/O ₃	0,1%/20ppm	10:00			
6	HF/HCl	0,2%/2%	02:00			
7	Rinse		01:00	11,4	51,4	Cleaning P-diff (3)
8	Rinse		00:15	2,9	2,9	

When now mixing all the components (see Table 7) and neutralizing them, it becomes obvious that the total volume is reduced by about 40%. The concentrations are in a similar range, except for fluoride, which is further reduced.

Table 7: Mixture concentrations and volumes of Ecosolar 1 scenario.

	buffer tank rinse pre rinse (1)	buffer tank texture (2)	buffer tank cleaning P- diff (3)	mixing tank total	mixing tank total
	per 50 wafers	per 50 wafers	per 50 wafers	per 100 wafers	per 100 wafers
pH value	5,62	10,50	3,55	10,00	7,00
conductivity [μ S/cm]	0,93	87,70	119,00	43,10	30,60
fluoride [mg/L]	-	-	0,87	0,30	0,30
chloride [mg/L]	-	-	8,95	3,09	6,81
potassium [mg/L]	-	12,80	-	8,14	8,14
volume [L]	2,85	100,00	54,29	314,27	314,27

4 CONCLUSIONS

4.1 Saved water volume

When comparing only the consumed rinsing water per batch (of 100 wafers) as it is done in Figure 8, a decrease in rinsing water volume is obtained compared to the industrial process. The overall rinsing volume is taken from the midterm LCA from this project. A detailed analysis of the industrial rinsing water is planned. For the ISC Konstanz consumptions, further reduction when employed in industrial environment is likely, as the ISC line has not been optimized for water saving (by applying rinsing cascades).

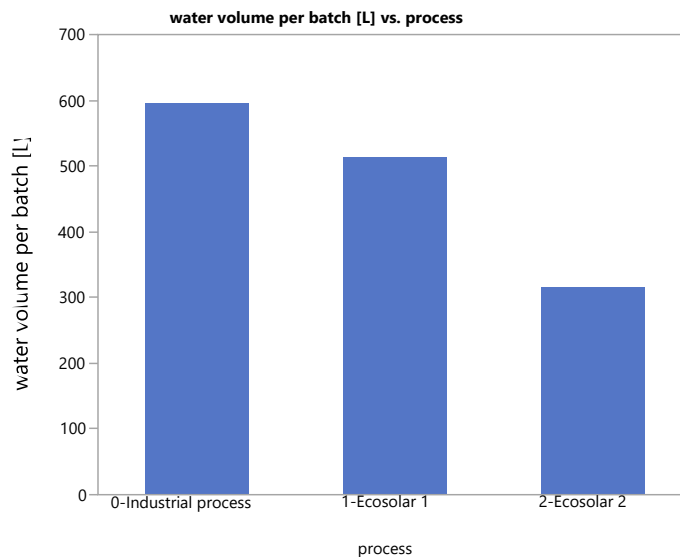


Figure 8: Rinsing water consumption per batch for the 3 regarded scenarios. The data for the industrial process have been provided by SoliTek.

As the concentrations of the rinsing water are low enough to reintroduce the water into the second step of the water purification system, the whole rinsing water from the scenarios Ecosolar 1 and Ecosolar 2 can be reused, yielding in 100% reduction of water consumption when only considering the rinsing water.

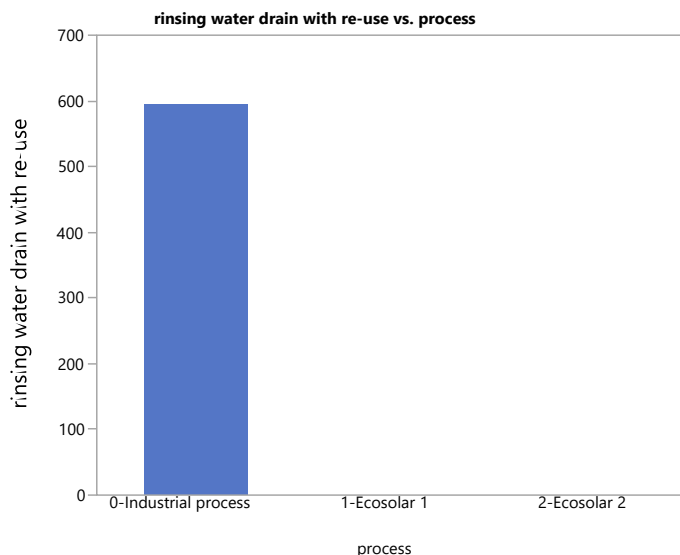


Figure 9: Rinsing water consumption per batch for the 3 regarded scenarios when taking reuse into account

4.2 Including the bleed volume from process baths

In addition to the rinsing water, further waste (water) is produced in every process bath, as the baths need to be replenished in order keep the concentration constant, to compensate for loss in chemical reaction or water carried into the bath from the previous rinsing step. Typically, around 2 – 4 % of the process bath volumes are replaced by fresh chemicals of the same (in case of the cleaning baths) or higher concentrations (in case of etchings baths). In addition to that the process baths are commonly exchanged after more than 100 batches. However, when dividing this additional waste water volume by the total number of batches only a small overall value of additional waste water is obtained. Table 8 and Table 9 summarizes the volumes required for rinsing. In addition, typical Feed and Bleed volumes and the cumulative amount of volume per batch for bath changes and are added and summed up.

Table 8: Ecosolar 1 sequence of process steps including processing times and rinsing volumes scaled for 100 wafers, bath volume 80L.

	process step	Concentrations employed	time [min]	Typical Feed/Bleed volume ranges [L]	water consumption [L]	Virtual buffer tanks
0	Start		0			
1	Rinse		00:15		5,8	Pre-rinse
2	KOH/H2O2	1,6%/1%	05:00	1,6 – 3,2		
3	Rinse		05:00		194	Pre-clean (1)
4	Rinse		00:15		5,8	
5	alkaline Tex (KOH/add)	2%/0,1%	13:00	1,6 – 3,2		
6	Rinse		05:00		194	texturing (2)
7	Rinse		00:15		5,8	
8	HF/O3	0,03%/20ppm	10:00	1,6 – 3,2		
11	HF/HCl	1,8%/2%	02:00	1,6 – 3,2		
12	Rinse		01:00		102,8	Cleaning P-diff (3)
13	Rinse		00:15		5,8	
Sum of volumes				6,4 – 12,8	513	
Volume bath change every 100 batches (per batch)				3,2		
Total extra volume (4% bleed, 10% of total for neutralization)				17,6		

Table 9: Ecosolar 2 sequence of process steps including processing times and rinsing volumes scaled for 100 wafers, bath volume 80L.

	process step	Concentrations employed	time [min]	Typical feed/bleed volume ranges [L]	water consumption [L]	Virtual buffer tanks
0	Start		0			
1	Rinse		00:15		5,8	Pre-rinse
2	alkaline Tex (KOH/add)	2%/0,1%	13:00	1,6 – 3,2		
3	Rinse		05:00		194	texturing (2)
4	Rinse		00:15		5,8	
5	HF/O3	0,03%/20ppm	10:00	1,6 – 3,2		
6	HF/HCl	1,8%/2%	02:00	1,6 – 3,2		
7	Rinse		01:00		102,8	Cleaning P-diff (3)
8	Rinse		00:15		5,8	
Sum of volumes				4,8 – 9,6	314	
Volume bath change every 100 batches (per batch)				2,4		
Total extra volume (4% bleed, 10% of total for neutralization)				13,2		

Overall, the water consumption of the rinses outnumbers the bleed and bath disposal volumes by far. For the current scenario we are calculating with the most conservative numbers: 4% bleed, batch change every 100 batches) and an additional volume of 10% required for neutralization. Despite this fact Figure 10 shows the immense water savings that can be achieved, when reusing the rinsing water from the wet chemical process steps. About 97% reduction of water consumption is easily possible for the Ecosolar 1 process. When reducing the overall water consumption, this ration goes down slightly to 96%.

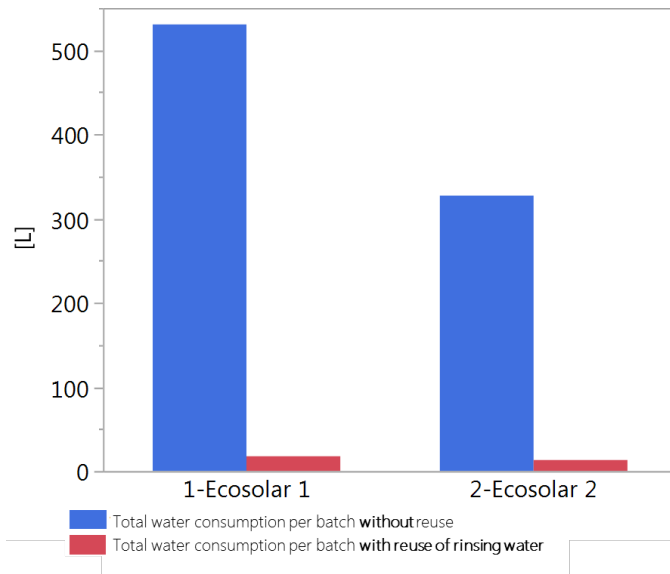


Figure 10: Waste water for the two process with (blue) and without rinsing water re-use (red).

4.3 Summary and outlook

We have shown that using the Ecosolar scenarios 96 – 97% of the waste water can be easily re-introduced into the water purification system without any further treatment than neutralization. When moving to a 100% quota for reuse of water the waste water treatment needs to become significantly more advanced, as chemical concentrations (such as organic additive or fluoride) in the bleed and bath change solutions are much higher. However, as waste water treatment has been necessary in the past anyhow, only small alterations are expected to be required to achieve full reuse of the DI water in existing production lines.

5 LITERATURE

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