Supporting Information

Recycling perovskite solar cells to avoid lead waste

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Materials and Methods

Scanning electron microscopy images were acquired on a JEOL JSM-6500F microscope. The cross-sections were freshly cut directly before the measurement. The investigation of the elemental composition was performed by energy dispersive X-ray (EDX) analysis with an EDX-detector from OXFORD INSTRUMENTS.

The X-ray diffraction patterns of the PbI₂ powder were obtained on a STOE powder diffractometer in transmission geometry (Cu K α_1 , $\lambda = 1.5406$ Å) equipped with a position-sensitive Mythen-1K detector. X-ray diffraction analysis of perovskite films was carried out in reflection mode using a Bruker D8 Discover with Ni-filtered Cu K α_1 -radiation ($\lambda = 1.5406$ Å) and a position-sensitive semiconductor detector (LynxEye).

¹H-NMR measurements were performed using a Bruker WM-400, 400 MHz. The PbI_2 was dissolved in DMSO-d6 and the recorded spectra were referenced to the solvent (DMSO-d6: ¹H, 2.50 ppm) relative to TMS.

Steady-state UV-Vis absorption spectra were acquired with a Lambda 1050 UV-Vis spectrophotometer (Perkin Elmer) using an integration sphere.

Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements were carried out using a Varian Vista RL.

J-V curves were recorded with a Keithley 2400 source meter under simulated AM 1.5G sunlight, with an incident power of approximately 100 mW cm⁻², which was corrected for the exact light intensity using a Fraunhofer ISE certified silicon cell. The reported device characteristics were estimated from the measured *J-V* curves obtained from the backwards scan (from V_{OC} to J_{SC}). All our devices show a significant amount of hysteresis between the forward and backwards scan,

which is comparable for all prepared samples. The active area of the solar cells was defined with a square metal aperture mask of 0.0831 cm^2 .

Photovoltaic device preparation

All materials where obtained from commercial sources and used as received, unless stated otherwise.

Solar cell preparation:

Fluorine doped tin oxide (FTO) coated glass sheets (7 Ω /sq, Pilkington, USA) were patterned by etching with zinc powder and 3 M HCl. They were subsequently cleaned with a 2 % Hellmanex solution and rinsed with de-ionized water, ethanol and acetone. Directly before applying the blocking layer, last organic residues were removed by an oxygen plasma treatment for 5 minutes. The dense TiO₂ layer was prepared from a sol-gel precursor solution by spin-coating onto the substrates and calcining at 500 °C in air.¹ For the sol-gel solution a 27.2 mM solution of HCl in 2-propanol was added dropwise to a vigorously stirred 0.43 mM solution of titanium isopropoxide (99.999 %, Sigma-Aldrich) in dry 2-propanol. The solution remained clear during the addition and was discarded otherwise. After cooling down, the substrate was transferred to a nitrogen-filled glovebox. A solution consisting of PbI₂ (1.25 M) and methylammonium iodide (1.25 M) in DMF was spin-coated dynamically (at 5000 rpm, total 15 s) onto the substrate. After 5 s, 100 μ L of chlorobenzene was added on top of the spinning substrate and afterwards the substrate was placed on a hotplate (100 °C for 10 min). After cooling down to room temperature, the films were covered with a layer of spiro-OMeTAD (Borun Chemicals, 99.5 % purity). For this purpose, spiro-OMeTAD was dissolved in 1 mL chlorobenzene. The solution was filtered and 10 µl 4-*tert*-butylpyridine (tBP) and 30 µl of a 170 mg/mL bis(trifluoromethane)sulfonamide lithium salt (LiTFSI) solution in acetonitrile were added. This solution was spin-coated dynamically at 1500 rpm for 45 s. The devices were stored overnight under air at room temperature and <30 rel% humidity to allow for oxidation of the spiro-OMeTAD. The top electrode was deposited by thermal evaporation of gold under vacuum (at $\sim 10^{-6}$ mbar), with a thickness of 40 nm.

Recycling of the solar cells:

In the first step the gold top electrode was removed with scotch tape, which was lightly pressed on the surface of the solar cell before pulling off. Alternatively, the gold can be removed by dissolving the hole transporter as described below, which resulted in delamination of the gold electrodes. Afterwards the gold can be collected via filtration.

The removal of the hole-transporter was done by immersing the whole substrate in chlorobenzene while slowly swirling the solution. After 1 min. the substrate was removed from the solution and was dried under a nitrogen stream. As a more environmentally friendly alternative to chlorobenzene, ethyl acetate can be used as solvent to remove the hole transporter using the same protocol as describe above.

In order to extract the methylammonium iodide from the perovskite, the surface of the substrate was dipped in distilled water for approximately 1 second and dried under a nitrogen stream afterwards. To evaporate the residual water, the substrate was placed on a hot plate at 100 °C for 10 min.

The obtained PbI₂ layer was immersed for 40 s in DMF to dissolve the PbI₂. The concentration of this solution was studied by UV-Vis spectroscopy (for more details see Figure S2). This solution was used for recycling the PbI₂. For the recycled and recrystallized batch of PbI₂, the DMF was removed under vacuum. The solids were dissolved in refluxing water and the solution was filtered to remove insoluble particles. The solution was slowly cooled down to 4 °C resulting in the crystallization of the PbI₂ as golden flakes. The PbI₂ was collected by filtration and dried

under vacuum prior to use. The PbI_2 solutions of the recycled and recrystallized PbI_2 looked clear and bright yellow.

The glass/FTO/TiO₂ substrate resulting from the above removal steps was placed in a fresh DMF bath for at least 4 min to remove the TiO_2 layer, after which the FTO substrate was dried at 100 °C. After cooling down, the FTO/glass substrate can be used for the preparation of new devices.

Cost estimation of perovskite based solar cell

We estimated the cost of the different layers in a perovskite-based solar cell with planar architecture. In order to make a realistic comparison between the different layers, the price of the chemicals was taken for large lab-scale quantities from different commercial suppliers. In this cost estimation we omitted the solvents since their cost contribution is expected to be negligible. Also the energy needed for the preparation is not included in the calculations, expect for the heating step in the TiO₂ blocking layer, which was annealed at 500 °C. We note that this is a very rough estimation, and upscaling of the production of perovskite solar cells is expected to have a significant influence on the price of starting materials. Nevertheless, the estimated costs can be used as a guide pointing out which layers are the most promising to recycle from an economical point of view.

Gold

We assume a 40 nm thick gold layer and no loss during the process. With the current gold price $(32.414 \notin kg \text{ in December 2015})$ this results in a price of 25 $\%m^2$.

HTM (Spiro-OMeTAD)

The calculation for the hole transporting material spiro-OMeTAD has been published by Petrus *et al.* and was estimated to be 40 $\text{m}^{2.2}$

Perovskite (MAPbI₃)

We assume a layer thickness of 300 nm and a density of the perovskite³ of 4.092 g/cm³, which results in a weight of $1.23 \cdot 10^{-3}$ kg/m². Assuming a full conversion of PbI₂ and MAI into MAPbI₃, and a cost of 915 \$/kg for PbI₂ (Fisher Chemicals) and of 850 \$/kg for MAI (DyeSol), results in a cost of 898 \$/kg. This results in a cost of 1.10 \$/m² for the perovskite layer.

Blocking layer (TiO₂)

The price for the titanium (IV) isopropoxide precursor is 3,336 \$/kg (Sigma Aldrich). The thickness of the TiO₂ is assumed to be 20 nm and the density $3.89 \cdot 10^3 \text{ kg/m}^{3,4}$ resulting in a cost of $0.31 \text{ $/m^2$}$. Additionally, we estimated the price for the calcination of the TiO₂ layer, since this is assumed to have a significant impact on the cost of this layer. For annealing on a lab-scale we used a hot plate (area 0.043 m^2) and measured the required energy for the heating step (0.9 kWh). With these values an energy demand of 20.8 kWh/m² was obtained, which was multiplied by the energy cost of 0.10 \$/kWh (assumed) resulting in a cost of 2.08 \$/m² for the heating step and a full price for the blocking layer of 2.39 \$/m².

FTO

The cost of FTO/glass strongly varies depending on the supplier; we found cost estimates in the range of 100-850 m^2 when ordered on a square meter scale. As we compare the lowest cost for lab scale we report a price of 100 m^2 for the FTO/glass substrate. That makes the substrate by far the most expensive layer within the solar cell stack.

As a result of the large price variations, we also requested a quote from Pilkington for industrial amounts of FTO/glass, in order to estimate a minimum cost. In this case the minimum price would be around 18 \$/m² when ordered in very large quantities. Despite the fivefold lower price when ordered at this scale compared to the lab scale, the FTO/glass is still among the most expensive layers. And while low-cost alternatives for the hole transporter and top electrode are under development and being published, there is only little progress in replacing the FTO/glass substrate with low-cost alternatives. This emphasizes the potential of recycling the FTO/glass substrate.

Analysis

The solvents used for the recycling could get contaminated with other materials. In example, the water layer containing the MAI could contain traces of lead, since PbI_2 is slightly soluble in water (0.0756 g/100 mL at R.T.). Here we analyzed the purity of the different fractions using different techniques.

NMR spectroscopy on recovered PbI₂

Figure S1 shows the ¹H-NMR spectrum of the recycled PbI_2 in DMSO-d₆ and MAI as reference. The recycled PbI_2 spectrum does not show any traces of the hole transporting material or the methylammonium iodide.

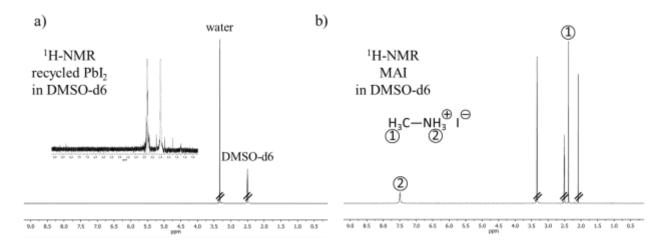


Figure S1. ¹H-NMR spectra of recycled PbI₂ (a) and MAI as reference (b) both in DMSO-d₆.

UV-vis measurements on solutions

The solvents used for recycling of the solar cells were studied using UV-vis and the results are presented in Figure S2. For these measurements 225 cm² of solar cells were recycled. 14 mL of chlorobenzene was used to remove the Spiro-OMeTAD, 14 mL of water to remove the MAI and 14 mL of DMF to remove the PbI₂.

The chlorobenzene solution was diluted 20 times and clearly showed the absorption of Spiro-OMeTAD and its oxidized species, which gives a signal in the range of 450-550 nm. MAI and PbI_2 are considered to be insoluble in chlorobenzene.

The water solution containing the MAI did not show any absorption in the range from 350-800 nm and a small onset near 300 nm. A small increase in the absorption is measured near 300 nm, which we assume to originate from PbI₂, however, this signal hardly exceeds the noise. As reference two solutions containing 0.25 mg mL⁻¹ and 0.075 mg mL⁻¹ lead iodide have been added to the spectrum. These reference solutions absorb stronger at 300 nm than our solution, indicating that the PbI₂ concentration is below 0.075 mg mL⁻¹. The noise in the signal does not allow more precise analyses of the concentration of PbI₂ in this sample. We ascribe the low concentration of the lead iodide in the water, to the rather low temperature of the water (~20 °C) and very short immersion time.

The DMF solution containing PbI_2 showed an absorption with an onset around 410 nm. No absorption in the range of 450-550 nm was observed, indicating the absence of (oxidized) Spiro-OMeTAD.

We prepared a calibration line of PbI₂ in DMF to determine the concentration of the solution. The absorption of the DMF solution from the recycling is marked with a blue circle in the graph (Figure S2d). The recycled solution has a concentration of 1.47 mg PbI₂ per mL of DMF. In total 14 mL of DMF was used for recycling 225 cm² of perovskite solar cell, which results in a recovery of 20.6 mg. Since the layer thickness is 300 ± 21 nm, we calculated the recovery rate of the PbI₂ to be $100 \pm 7\%$. We like to point out that the error in the (measured) layer thickness is relatively large, and therefore the error in the recovery rate is also relatively high. Nevertheless we show that the PbI₂ can be recovered quantitatively.

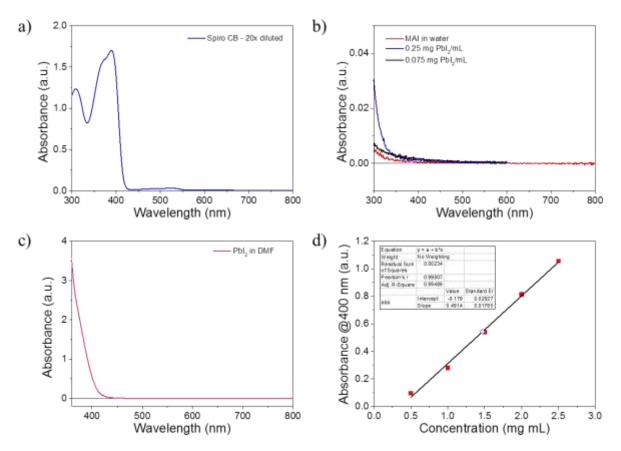


Figure S2: UV-vis absorption spectra of a) the chlorobenzene fraction (diluted 20 times) containing Spiro-OMeTAD, b) the water fraction containing the extracted methyl ammonium iodide and traces of PbI₂, c) The DMF fraction containing lead iodide and d) the calibration line to determine the lead iodide concentration of the recovered PbI₂. The blue circle indicates the recycled DMF solution.

ICP measurement on solutions.

The solutions used for the UV-vis experiments were also used for the ICP measurements. The chlorobenzene was removed from the recovered Spiro-OMeTAD under vacuum and then the possibly present PbI₂ was dissolved in 15 mL of water. The recovered MAI solution in water was measured without workup. The DMF was removed from the recovered PbI₂ under vacuum and the solids were redissolved in 55 mL of water. These solutions were measured with ICP to check for the presence of lead and titanium.

The concentration of titanium in all samples was below the detection limit ($<0.004 \ \mu g \ mL^{-1}$), indicating that the electron blocking layer does not dissolve during the recycling process and is simply delaminated. This is also expected since TiO₂ is considered insoluble in these solvents.

The concentration of lead was determined at two different wavelengths (214 and 220 nm). The chlorobenzene fraction used to remove the Spiro-OMeTAD practically contains no lead. The measurement at 217 nm showed no detectable amount of lead, while the measurement at 220 nm resulted in a concentration just above the detection limit of 0.068 μ g mL⁻¹.

According to ICP measurements the water fraction used for extraction of MAI contains 4.22 to $4.35 \ \mu g \ mL^{-1}$ lead. This is in agreement with the UV-vis absorption measurements, which indicated that the concentration would be below 75 $\mu g \ PbI_2 \ mL^{-1}$. We ascribe the very low concentrations of lead in the water to the short immersion time and relatively low solubility of PbI₂ in water. Additionally we like to point out that the concentration of lead in the water is strongly influenced by the amount of water used (in our experiments around 700 mL per square meter of solar cell). Water containing 5 $\mu g \ mL^{-1}$ lead or more are considered hazardous according to the US Environmental Protection Agency (EPA, Federal Hazardous Waste code D008).⁵ The water fraction containing the recovered MAI is therefore below the maximum concentration of contaminants for toxicity characteristic according to EPA.

For the DMF fraction, which was used for extraction of the lead iodide, concentrations of 155.1 to 157.4 μ g Pb mL⁻¹ were measured. This would result in a total recovery of 19.0 - 19.3 mg PbI₂ for 225 cm² of solar cell (92 – 94%). Comparable to the results from the UV-vis experiments, a near quantitative recovery rate was obtained.

Solution	$Pb_{217 nm} (\mu g m L^{-1})$	$Pb_{220 nm} (\mu g m L^{-1})$	$Ti_{335 nm} (\mu g m L^{-1})$	$Ti_{336 nm} (\mu g m L^{-1})$
Chlorobenzene	<l.o.d.< td=""><td>0.068</td><td><l.o.d.< td=""><td><l.o.d.< td=""></l.o.d.<></td></l.o.d.<></td></l.o.d.<>	0.068	<l.o.d.< td=""><td><l.o.d.< td=""></l.o.d.<></td></l.o.d.<>	<l.o.d.< td=""></l.o.d.<>
Water	4.22	4.35	<l.o.d.< td=""><td><l.o.d.< td=""></l.o.d.<></td></l.o.d.<>	<l.o.d.< td=""></l.o.d.<>
DMF	157.4	155.1	<l.o.d.< td=""><td><l.o.d.< td=""></l.o.d.<></td></l.o.d.<>	<l.o.d.< td=""></l.o.d.<>
Detection limit	0.090	0.040	0.004	0.005

 $\label{eq:sigma} \textbf{Table S1}: \mbox{ Metal concentrations measured by ICP in different fractions}.$

L.O.D. = limit of detection

Recycling glass/FTO/TiO₂ substrate

Initially recycling of the glass/FTO/TiO₂ substrate was attempted after removing the PbI_2 by immersing in DMF. The decrease in PCE over several recycling steps indicated an issue with recycling the TiO₂ layer. XRD measurements confirmed degradation of the TiO₂ layer by immersing in DMF.

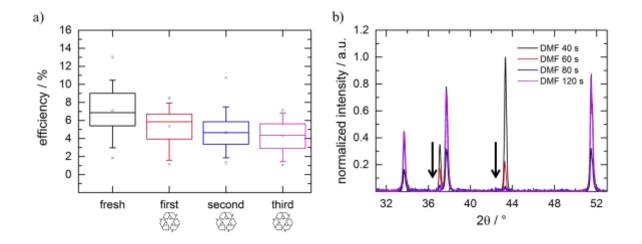


Figure S3. Box plot of the PCEs for the devices prepared on fresh and recycled $TiO_2/FTO/glass$. The box plot displays the average, median, minimum, maximum and 75 and 95% deviation, respectively (a). XRD pattern of FTO/TiO₂ substrates immersed into DMF for different times (b). The decrease of the TiO₂ reflections is illustrated with two black arrows.

Additionally to XRD measurements, SEM top view images of a freshly prepared FTO-TiO₂ and a recycled FTO substrate were prepared (Figure S4). A slight difference in contrast is visible which can be attributed to the TiO₂ layer on top. In order to verify this observation, energy dispersive X-ray spectroscopy (EDX) was performed. The substrate containing the TiO₂ blocking layer showed the presence of titanium on the sample surface (Figure S4). In contrast, on the recycled FTO substrate no titanium was observed, indicating the complete removal of the blocking layer.

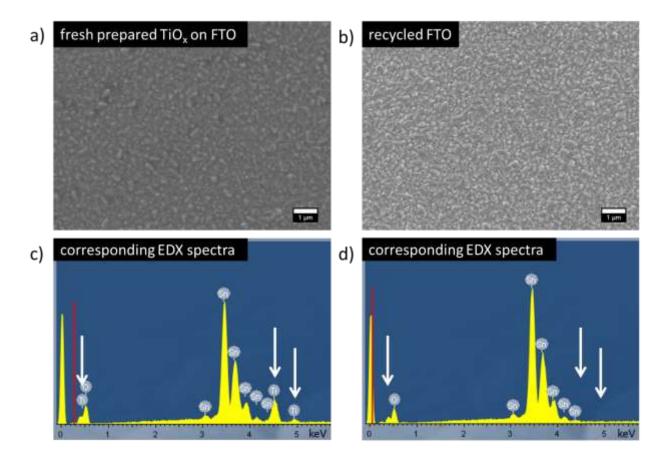


Figure S4: SEM top view image of a FTO-TiO₂ substrate (a) and a recycled FTO substrate (b) and the corresponding EDX spectra (c-d). The white arrows mark the peaks of Ti.

The transmittance of the substrate was studied by UV-vis absorption for fresh FTO, FTO with TiO_2 and recycled FTO and the results are presented in Figure S5. The transmittance for all films is around 80% for most of the visible spectrum. The thin layer of TiO_2 , most clearly affects the spectrum in the region of 350-500 nm. On the recycled substrate the TiO_2 was successfully removed as can been seen in the transmission spectrum.

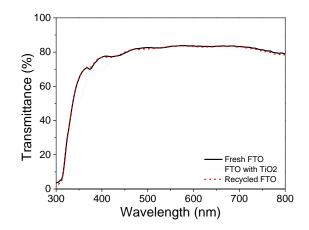


Figure S5: Transmittance spectra of fresh FTO, FTO with TiO₂ and recycled FTO substrates.

In order to see the effect of the DMF treatment on the TiO_2 , cross-sections of a 600 nm thick blocking layer were analyzed by SEM. The extra-thick blocking layer was prepared by spincoating several layers using the standard sol-gel approach with heating steps (150 °C/10 min) in between. One of these samples was afterwards immersed in DMF for 3 min and dried at 100 °C. In Figure S6 the images of both a DMF treated and a non-treated sample are shown. The SEM images indicate that the DMF delaminates the TiO_x layer by infiltrating the interface. Further studies regarding the delamination process are ongoing.

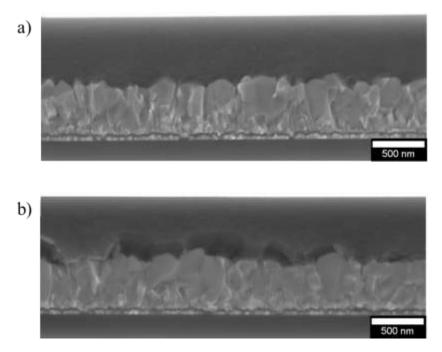


Figure S6. Cross-sections of non-calcined TiO_x blocking layers before (a) and after the DMF treatment (b).

Recycling FTO/glass, photovoltaic performance

After removing the TiO_2 blocking layer by immersing the substrate in DMF, the substrates were used to prepare fresh devices. Good PCEs with a high reproducibility were obtained, indicating the successful recycling of the FTO/glass substrate.

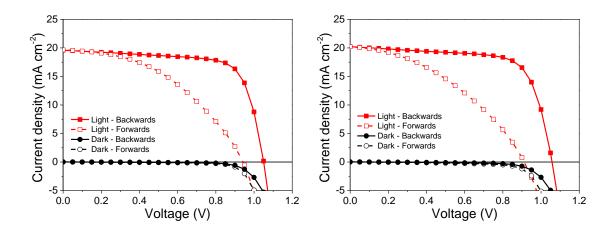


Figure S7: *J-V* curves of the record cells on fresh FTO and 3x recycled FTO, showing no significant differences in the hysteresis or the dark measurements.

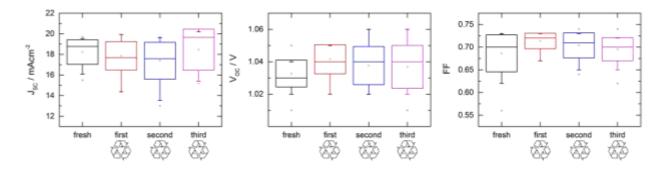


Figure S8. Box plot of the J_{SC} , V_{OC} and FF with displaying the average, median, minimum, maximum and 75 and 95% deviation of solar cells prepared on fresh, one, two and three times recycled FTO, respectively.

Table S2: Device performance of device	ce after recycling the FTO/glass substrate	over various cycles.

Freshly prepared	$J_{\rm SC}$ / mAcm ⁻²	PCE / %	$V_{\rm OC}$ / V	FF
Average values	18.2	13.0	1.03	0.69
Standard deviation	1.2	1.1	0.01	0.04
Best cell	19.2	14.6	1.03	0.73
Shorted cells	2 out of 24			

First recycling	$J_{\rm SC}$ / mAcm ⁻²	PCE / %	$V_{\rm OC}$ / V	FF
Average values	17.9	13.4	1.04	0.71
Standard deviation	1.4	1.1	0.01	0.02
Best cell	19.6	15.1	1.05	0.72
Shorted cells	5 out of 24	ł	ł	I

Second recycling	$J_{\rm SC}$ / mAcm ⁻²	PCE / %	$V_{\rm OC}$ / V	FF
Average values	17.4	12.8	1.04	0.70
Standard deviation	1.8	1.3	0.01	0.03
Best cell	19.6	14.7	1.03	0.72
Shorted cells	3 out of 24	1	1	-

Third recycling	$J_{\rm SC}$ / mAcm ⁻²	PCE / %	$V_{ m OC}$ / V	FF
Average values	18.5	13.5	1.04	0.70
Standard deviation	2.0	1.5	0.01	0.03
Best cell	20.2	15.4	1.06	0.71
Shorted cells	2 out of 24		-	•

Estimation of lead content in solar parks

As shown in the cost estimation above, each square meter of solar panel would contain approximately 1.2 g of perovskite absorber. MAPbI₃ consist of 34 wt% lead, which leads to a lead content 0.42 g/m² solar cell. When considering a single solar park, which can easily exceed more than 200 hectares (2 x 10^6 m²), the lead content will be over 800 kg.

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