

**FATE OF END-OF-LIFE SOLAR PHOTOVOLTAICS IN
DIFFERENT ENVIRONMENTAL SCENARIOS AND
PROVIDING RISK ASSESSMENT FRAMEWORK**

PREETI NAIN



**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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PROVIDING RISK ASSESSMENT FRAMEWORK**

by

PREETI NAIN

Department of Civil Engineering

Submitted

**in fulfilment of the requirements of the degree of Doctor of Philosophy
to the**



INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER 2021

Dedicated to

my parents,

my husband, Manish

and

my son, Niom

Thesis Certificate

This is to certify that the thesis entitled “**Fate of End-of-life Solar Photovoltaics in different Environmental Scenarios and providing Risk Assessment Framework**” submitted by **Preeti Nain** to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** is a bona fide record of research work carried by her under my supervision. The content of this thesis in full, or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Prof. Arun Kumar



Department of Civil Engineering

Indian Institute of Technology, Delhi

Haus Khas, New Delhi-110016

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List of Abbreviations

Abbreviation	Description	Abbreviation	Description
PV	photovoltaic	Al	aluminium
EoL	end-of-life	Ag	silver
IMC	initial metal content	As	arsenic
LRC	leaching rate constant	B	Boron
SPV-LPI	solar PV metal-associated leachate pollution index	Cd	Cadmium
MSW	municipal solid waste	Co	Cobalt
CdTe	cadmium telluride	Cr	Chromium
CIGS	copper indium gallium diselenide	Cu	Copper
a-Si	amorphous-silicon	Fe	Iron
c-Si	crystalline-silicon	Ga	Gallium
GaAs	gallium arsenide	In	Indium
OPV	organic PV	Mg	magnesium
PERC	passivated emitter and rear cell	Mn	manganese
CZTS	copper zinc tin sulphide	Mo	molybdenum
IEA	International energy agency	Ni	Nickel
WEEE	waste electrical and electronic equipment	P	phosphorus
EIA	environment impact assessment	Pb	lead
TCLP	toxicity characteristic leaching procedure	Sb	Antimony
WET	waste extraction test	Si	Silicon
T ₉₀	time required for 90% leaching of metals	Se	Selenium
PoE	probability of exceedance	Sn	Tin
RFID	Radio-frequency identification	Te	Tellurium
REI	Renewable Energy India Expo	Ti	Titanium
MLF	Metal loss factor	Zn	Zinc
TGSC	Third generation solar cells	TOC	Total Organic Carbon
MHS	Metal Hazard Score	RPN	Risk Priority Number
RoHS	Restriction of Hazardous Substances	FTA	Fault Tree Analysis
DRAS	Delisting Risk Assessment Software	UV	Ultraviolet
RfD	Oral reference dose	GHG	greenhouse gas
CSF _o	Oral cancer slope factor	LCA	life cycle assessment
DAF	Dilution attenuation factor	EPBT	energy payback time
HHRA	Human Health risk assessment	BOS	balance of system
ANOVA	Analysis of variance	EVA	ethyl vinyl acetate
REI	Renewable Energy India	TOC	Total organic carbon
FSGP	First and second generation photovoltaics		

Abstract

The declining cost of manufacturing materials, sharp depletion of fossil fuels, and increasing energy demand resulted in exponential growth of photovoltaic market. This raises the concern regarding the management of the massive waste volume when their operational life is completed. Alarm stems from both the volumes of the waste stream and the potentials for environmental toxicity associated with the hazardous metals present in some PVs, if damaged not managed properly or dumped in landfills leading to serious environmental concerns. Considering this, the present thesis addressed this concern by investigating the following questions: (1) What is the risk posed by PVs to environment and human health based on material composition? 2) What is the leaching behaviour of PVs as per standard waste characterization tests and in realistic landfill/environmental conditions? 3) What are the factors affecting effective PV waste management from stakeholder's perspectives? 4) What are manufacturers and consumers perspectives regarding handling of PV waste.

In present thesis, the literature review of 300 studies was done to compile information on material composition of various PVs which was used to estimated leaching rates and leaching rate constants in various environmental matrices. The compiled material composition data and leaching rates were applied to estimate the leachate composition resulting on hypothetical dumping of PVs in environment. The fate and transport methodology was applied on resulting leachate for estimating the exposure point concentrations of various leached metals in soil and groundwater. Further, the ecological and human health risk was assessed for children and adult. The results indicated that the children are at highest risk, mainly due to lead. Metals, such as cadmium, lead, indium, molybdenum and tellurium pose maximum risks for child and adult sub-populations via soil-dermal pathway followed by soil-ingestion pathway. This is further proved by calculated high values of contamination factor and geo- accumulation index for cadmium (102.4), indium (238.9) and molybdenum (16.12).

After theoretical estimation of leaching rates and risk, short-term and long-terms experiments were performed to investigate the leaching behavior of first- and second-generation PVs in realistic environmental conditions (MSW leachate) and as per standard waste characterization tests (short-term) respectively. A one-year leaching study was performed using 15*15 cm² size modules pieces in broken and unbroken conditions exposed to three synthetic solutions of pH 4, 7, 10 and one real MSW landfill leachate. Results indicated that rainwater was found to be predominant for metal release from silicon-based PV, with silver, lead and chromium being

released up to 27%. CIGS PV was found to be least vulnerable in various conditions with negligible metal release. The maximum metal release observed in the present study is 30% of the initial amount under the most stressful conditions and minimal metals were released in real landfill leachate. The findings from short term batch leaching tests indicated that extractions using landfill leachates resulted in lower metal release than standard methods. The leached metal concentrations were found to be within the threshold limits except for cadmium, copper, lead and selenium, with maximum lead release from amorphous-PV. Regardless of small size (1–2 cm pieces) and agitation, Germany and Japan's standard tests resulted in minimal release except of copper from CIGS PV. For all scenarios, increased metal release was observed with decrease in sample size and increase in leachate dilution and thus, leaching in highly acidic conditions are by no means representative for modules dumping in realistic conditions.

With respect to third generation solar PVs, potential release values (in terms of loss factors) of various compounds used in different layers of cells in neutral water and landfill leachate conditions were estimated using a theoretical exercise. Top five compounds with highest metal release probability (probability > 0.5) were found to be: PbI_2 (highest LF) > CuI > $\text{Cd}(\text{OH})_2$ > CuSCN > CdO (smallest LF). Also, the identified compounds with lowest risk were: PbSe < Sb_2S_3 < CdSe < Al_2O_3 < SnS (lowest probability: 10^{-10} to 10^{-16}). With respect to solar cells, perovskite solar cells were ranked first and quantum dot solar cells were ranked second due in terms of hazard. Further, the organic and dye-sensitized solar cells are of least concern.

After investigating the leaching behaviour and risk posed by various PVs, stakeholder perception towards EoL PV waste management was investigated via a survey-based study. As per results, more than 90% of manufacturers were involved in crystalline-silicon PV business. Only 20% manufacturers replied when asked on the aspect of EoL modules, showing that the PV waste is comparatively a new subject and not enough discussion have been devoted to it. Lack of recycling infrastructure, incentives, and environmental awareness significantly influence recycling and reuse practices. The maximum probability of the material release from dumped solar panels was estimated to be 0.053. Risk priority number analysis suggests that damage resulting to metal leaching as the most significant event. At present, 76% producers do not recycle or reuse PV waste material, preferably sell them to informal waste recyclers or rag pickers. Findings from the present study highlight the urgency to develop a suitable system for collection and management of EoL modules.

सार

विनिर्माण सामग्रियों की घटती लागत, जीवाश्म ईंधन की तेज कमी और ऊर्जा की बढ़ती मांग के परिणामस्वरूप फोटोवोल्टिक बाजार में वृद्धि हुई। यह बड़े पैमाने पर सोलर फोटोवोल्टिक अपशिष्ट मात्रा के प्रबंधन के बारे में चिंता उठाती है। अपशिष्ट धारा की मात्रा और कुछ सोलर फोटोवोल्टिक में मौजूद खतरनाक धातुओं से जुड़ी पर्यावरणीय विषाक्तता की संभावना दोनों से उत्पन्न हो सकती है, अगर ठीक से प्रबंधित नहीं किया गया या लैंडफिल में डंप किया गया। इसे ध्यान में रखते हुए, वर्तमान थीसिस ने निम्नलिखित प्रश्नों की जांच करके इस चिंता को संबोधित किया गया है: (1) भौतिक संरचना के आधार पर फोटोवोल्टिक द्वारा पर्यावरण और मानव स्वास्थ्य के लिए जोखिम क्या है? 2) मानक अपशिष्ट लक्षण वर्णन परीक्षणों और यथार्थवादी लैंडफिल/पर्यावरणीय परिस्थितियों में फोटोवोल्टिक का लीचिंग व्यवहार क्या है? 3) हितधारक के दृष्टिकोण के अनुसार फोटोवोल्टिक अपशिष्ट प्रबंधन को प्रभावित करने वाले कारण क्या हैं? 4) फोटोवोल्टिक कचरे के प्रबंधन के संबंध में निर्माताओं और उपभोक्ताओं के दृष्टिकोण क्या हैं।

वर्तमान थीसिस में, विभिन्न फोटोवोल्टिक की भौतिकवाद संरचना के अनुसार जानकारी संकलित करने के लिए 300 साहित्य अध्ययनों की समीक्षा की गई थी, जिसका उपयोग विभिन्न पर्यावरणीय मैट्रिक्स में लीचिंग दर और लीचिंग दर स्थिरांक का अनुमान लगाने के लिए किया गया है। पर्यावरण में फोटोवोल्टिक के काल्पनिक डंपिंग के परिणामस्वरूप लीचेट संरचना का अनुमान लगाने के लिए संकलित सामग्री संरचना डेटा और लीचिंग दरों को लागू प्रयुक्त गया। मिट्टी और भूजल में विभिन्न निक्षालित धातुओं के जोखिम बिंदु सांद्रता का आकलन करने के लिए परिणामी लीचेट पर भाग्य और परिवहन पद्धति लागू की गई। इसके अलावा, बच्चों और वयस्कों के लिए पारिस्थितिक और मानव स्वास्थ्य जोखिम का आकलन किया गया। परिणामों ने संकेत दिया कि बच्चों को मुख्य रूप से लेड के कारण सबसे अधिक जोखिम है। कैडमियम, लेड, इंडियम, मोलिब्डेनम और टेल्यूरियम जैसी धातुएं मिट्टी-त्वचीय मार्ग के बाद मिट्टी-अंतर्ग्रहण मार्ग के माध्यम से बच्चे और वयस्क उप-आबादी के लिए अधिकतम जोखिम पैदा कर सकती हैं। यह आगे कैडमियम (102.4), इंडियम (238.9) और मोलिब्डेनम (16.12) के लिए संदूषण कारक और भू-संचय सूचकांक के उच्च मूल्यों की गणना से साबित होता है।

लीचिंग दरों और जोखिम के सैद्धांतिक आकलन के बाद, यथार्थवादी पर्यावरणीय परिस्थितियों (एमएसडब्ल्यू लीचेट) और मानक अपशिष्ट लक्षण वर्णन परीक्षण (लघु-अवधि) के अनुसार में पहली और दूसरी प्रकार के फोटोवोल्टिक का लीचिंग व्यवहार का अध्ययन अल्प अवधि और दीर्घावधि में किया गया। पीएच 4, 7, 10 और एक वास्तविक एमएसडब्ल्यू लैंडफिल लीचेट के तीन सिंथेटिक समाधानों में 15*15 सेंटीमीटर² आकार के सोलर फोटोवोल्टिक टुकड़ों को टूटी और अखंड

परिस्थितियों में लीचिंग अध्ययन किया गया। परिणामों से देखा गया कि सिलिकॉन आधारित फोटोवोल्टिक से मेटल रिलीज के लिए वर्षा जल प्रमुख कारण पाया गया, जिसमें सिल्वर, लेड और क्रोमियम 27% तक निथर हुए। सीआईजीएस फोटोवोल्टिक को नगण्य मेटल रिलीज के साथ विभिन्न स्थितियों में कम से कम कमजोर पाया गया। इस अध्ययन में देखा गया कि अधिकतम मेटल रिलीज सबसे तनावपूर्ण परिस्थितियों में प्रारंभिक राशि का 30% है और वास्तविक लैंडफिल लीचेट में न्यूनतम मेटल रिलीज पाया गया। शॉर्ट टर्म बैच लीचिंग परीक्षणों के निष्कर्षों से पाया गया कि लैंडफिल लीचेट्स का उपयोग करने वाले निष्कर्षणों के परिणामस्वरूप मानक विधियों की तुलना में कम मेटल रिलीज हुई। अम और फट्स-फोटोवोल्टिक से अधिकतम लेड रिलीज के साथ कैडमियम, कॉपर, लेड और सेलेनियम को छोड़कर बाकी सब लीचड मेटल की सांद्रता थ्रेशोल्ड सीमा के भीतर पाई गई। छोटे आकार (1-2 सेंटीमीटर के टुकड़े) और अजीटएसण के बावजूद, जर्मनी और जापान के मानक परीक्षणों के परिणामस्वरूप सीआईजीएस फोटोवोल्टिक से कॉपर को छोड़कर अन्य मेटल का न्यूनतम रिलीज हुआ। सभी परिदृश्यों के अनुसार, बढ़ी हुई मेटल रिलीज, नमूना आकार में कमी और कम केंद्रित लीचेट के साथ देखी गई थी और इस प्रकार, अत्यधिक अम्लीय परिस्थितियों में लीचिंग किसी भी तरह से वास्तविक परिस्थितियों में डंप किए हुए फोटोवोल्टिक के लिए प्रतिनिधि नहीं हैं।

तीसरी प्रकार के फोटोवोल्टिक के संबंध में, पीएच 7 और लैंडफिल लीचेट स्थितियों में फोटोवोल्टिक सेल की विभिन्न परतों में उपयोग किए जाने वाले विभिन्न मेटल के संभावित रिलीज मूल्यों (एलएफ-के रूप में) का सैद्धांतिक अभ्यास का उपयोग करके अनुमान लगाया गया। उच्चतम मेटल रिलीज संभावना (संभावना > 0.5) वाले पांच यौगिक: PbI_2 (उच्चतम एलएफ) > CuI > $Cd(OH)_2$ > $CuSCN$ > CdO (सबसे कम एलएफ)। इसके अलावा, सबसे कम जोखिम वाले पहचाने गए यौगिक थे: $PbSe$ < Sb_2S_3 < $CdSe$ < Al_2O_3 < SnS (न्यूनतम संभावना: 10^{-10} से 10^{-16})। सौर फोटोवोल्टिक सेल के संबंध में, पेरोव्स्काइट सौर सेल को पहले स्थान पर रखा गया और क्वान्टम डॉट सौर सेल को खतरे के मामले में दूसरा स्थान दिया गया। इसके अलावा, आंगिक और डार्क-सेंसिटीज्ड सौर सेल कम से कम चिंता का विषय हैं।

विभिन्न फोटोवोल्टिक द्वारा लीचिंग व्यवहार और खतरे की जांच के बाद, सर्वेक्षण-आधारित अध्ययन के माध्यम से फोटोवोल्टिक अपशिष्ट प्रबंधन के प्रति हितधारकों की दृष्टिकोण की जांच की गई। परिणामों के अनुसार, 90% से अधिक निर्माता क्रिस्टलाइन-सिलिकॉन फोटोवोल्टिक व्यवसाय में शामिल थे। फोटोवोल्टिक अपशिष्ट के पहलू पर पूछे जाने पर केवल 20% निर्माताओं ने उत्तर दिया, यह दर्शाता है कि फोटोवोल्टिक अपशिष्ट तुलनात्मक रूप से एक नया विषय है और इस पर पर्याप्त चर्चा नहीं की गई है। पुनर्चक्रण अवसंरचना का अभाव, प्रोत्साहन और पर्यावरण जागरूकता पुनर्चक्रण और पुनः उपयोग प्रथाओं को महत्वपूर्ण रूप से प्रभावित करती है। डंप किए गए सौर पैनलों से मेटल के निकलने की अधिकतम संभावना 0.053 होने का अनुमान लगाया गया।

जोखिम प्राथमिकता संख्या (आर.पी.एन.) विश्लेषण से पता चलता है कि सबसे महत्वपूर्ण घटना के रूप में मेटल लीचिंग है। वर्तमान में, 76 प्रतिशत उत्पादक फोटोवोल्टिक अपशिष्ट मेटल का पुनर्चक्रण या पुनः उपयोग नहीं करते हैं, अधिमानतः उन्हें अनौपचारिक अपशिष्ट पुनर्चक्रणकर्ताओं या कूड़ा बीनने वालों को बेचते हैं। वर्तमान अध्ययन के निष्कर्ष अनौपचारिक अपशिष्ट के संग्रह और प्रबंधन के लिए एक उपयुक्त प्रणाली विकसित करने की तात्कालिकता को उजागर करता है।