Dependence of Toxicity Test Results on Sample Removal Methods of PV Modules

by

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ABSTRACT

The volume of end-of-life photovoltaic (PV) modules is increasing as the global PV market increases, and the global PV waste streams are expected to reach 250,000 metric tons by the end of 2020. If the recycling processes are not in place, there would be 60 million tons of end-of-life PV modules lying in the landfills by 2050, that may not become a not-so-sustainable way of sourcing energy since all PV modules could contain certain amount of toxic substances. Currently in the United States, PV modules are categorized as general waste and can be disposed in landfills. However, potential leaching of toxic chemicals and materials, if any, from broken end-of-life modules may pose health or environmental risks. There is no standard procedure to remove samples from PV modules for chemical toxicity testing in the Toxicity Characteristic Leaching Procedure (TCLP) laboratories as per EPA 1311 standard. The main objective of this thesis is to develop an unbiased sampling approach for the TCLP testing of PV modules. The TCLP testing was concentrated only for the laminate part of the modules, as they are already existing recycling technologies for the frame and junction box components of PV modules. Four different sample removal methods have been applied to the laminates of five different module manufacturers: coring approach, cell-cut approach, strip-cut approach, and hybrid approach. These removed samples were sent to two different TCLP laboratories, and TCLP results were tested for repeatability within a lab and reproducibility between the labs. The pros and cons of each sample removal method have been explored and the influence of sample removal methods on the variability of TCLP results has been discussed. To reduce

the variability of TCLP results to an acceptable level, additional improvements in the coring approach, the best of the four tested options, are still needed.

To,

My father - Mr. Leslie Jose David, my mother – Dr. Shoba Leslie, my sister – Ms. Joanna Leslie, and my other family members and friends for their caring support and love without whom, my thesis work would have been impossible to complete.

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1. INTRODUCTION

1.1. Background

Solar photovoltaic (PV) deployment has grown exponentially since the early 2000s. PV modules offer economic and environmentally friendly electricity production but like any other technology, it ages and ultimately requires decommissioning [1]. Due to relatively low volumes of PV modules reaching end-of-life on a global scale, not much research into recycling of PV modules has been done. However, with the recent rise of utility-scale PV power plants, interest in PV recycling has been increasing. End-of-life PV modules waste is projected to increase to more than 60-78 million metric tons cumulatively by year 2050.

When these broken PV modules are landfilled and not recycled, they could pose environmental and health risks through leaching of toxic chemicals and materials, if any. PV modules may contain hazardous materials like lead, polybrominated diphenyl ether (PBDE), chromium and cadmium, which have the potential to contaminate ground and surface water, especially if large quantities of modules are disposed at a single landfill. This leaching of toxic materials takes place due to precipitation when landfilled and these toxic materials are exposed to soil and groundwater which contaminate them.

1.2 Problem Statement

As per the EPA regulations, there are four characteristics for hazardous wastes for land disposal: corrosivity, ignitability, reactivity and toxicity. The toxicity is defined by EPA 1311 method where the PV modules are subjected to Toxicity Characteristic Leaching

Procedure (TCLP) to determine the amount of toxic elements that can leach to the ground [2]. Elements regulated by the TCLP include arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. The validity of the TCLP test heavily depends on the location of removed samples in the module, specifically within the laminate area, and the particle size of the removed sample. Therefore, it is critical that the sample removal procedure is designed to avoid biased TCLP results. It is also important to comply with the EPA 1311 regulations. There are two main factors to comply with the EPA 1311 method: area (dimension) of the sample and the weight restriction. According to EPA 1311, *"Particle size reduction is required, unless the solid is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm standard sieve)".* Also, for TCLP testing, there is a sample weight restriction of 100-110g from the TCLP labs.

1.3 Objective

My main objective is to evaluate various sample removal methods of laminate. The frame and JCC (junction box, cables, and connectors) are not considered, as they are recyclable and reusable materials, and cost-effective recycling industries already exist for these components [3]. Sample removal procedures also should be reproducible within a single sample supplied to a lab, and across replicate samples supplied to multiple labs. In the laminate area, the presence of arsenic, barium, cadmium, chromium, selenium, silver, and mercury are zero or nor detectable by the testing laboratories. Only the presence of lead is considered as it is the only main toxic material that could be present in the crystalline silicon PV modules.

The motivation of my work is to reduce the variation in the TCLP results. This variation is caused mainly due to the following reasons:

- Sample removal locations from the laminate

- Particle size of the sample

- Glass coverage on the samples

- Crack lengths of the samples

The main objective of this study are as follows:

- To evaluate various PV module sample removal methods to ensure that TCLP results from recognized labs are unbiased, representative and accurate.

- To reduce the variability of the TCLP results, and shall be consistent to ensure that the TCLP results obtained using replicate samples are repeatable within a single TCLP laboratory and are reproducible between different TCLP labs.

- To demonstrate why samples tested for toxicity should not be of size greater than 9.5 mm and not crushed to sizes less than 1 mm or to micron level in the TCLP labs.

2. LITERATURE REVIEW

2.1 Need for PV Recycling

The growth in solar energy over the past decade has been nothing short of phenomenal. Newly installed capacity reached 50 GW/year in 2015 and 75 GW/year in 2016, leading to a cumulative capacity of 227 GW/year by 2015 as shown in Fig. 1 and 303 GW/year by 2016 [4].
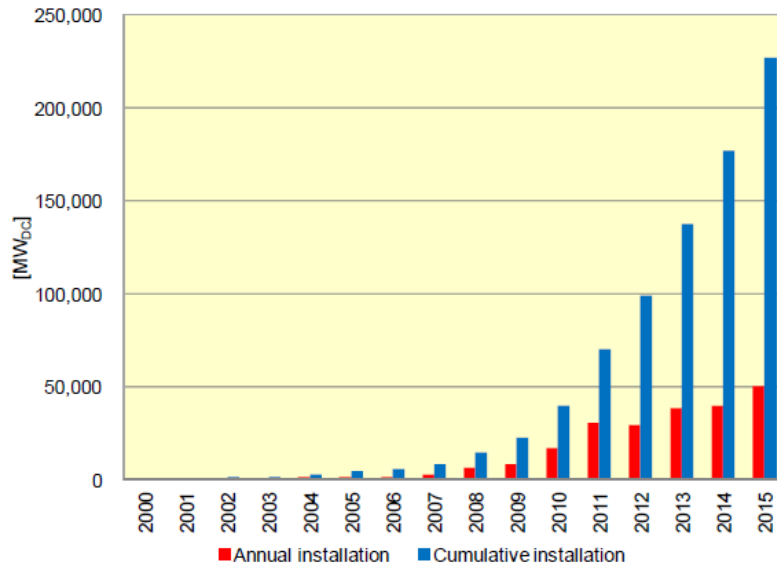
Fig. 1. Trends in PV installations around the world [4]

High cumulative deployment rates are expected by 2030 in China (1,731 GW), the United States (600 GW), Germany (110 GW), Japan (350 GW) and India (600 GW). As the PV market continues to grow, so will the waste even if it only appears after a relatively long-time delay. With the recently increased cell efficiencies and decreasing production costs,

the PV industry has grown tremendously and also the PV waste [5], with Fig. 2 showing

the global PV production in the decade from 1998 to 2038.
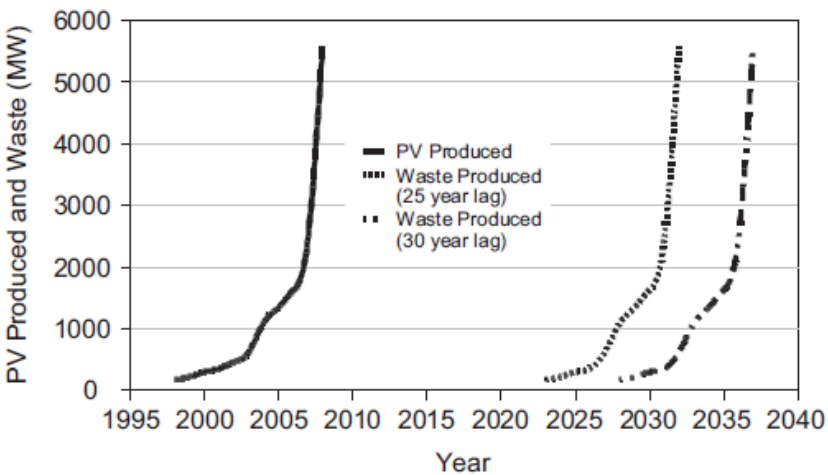
Fig. 2. Global PV production and projected waste from 1998 to 2038 [5]
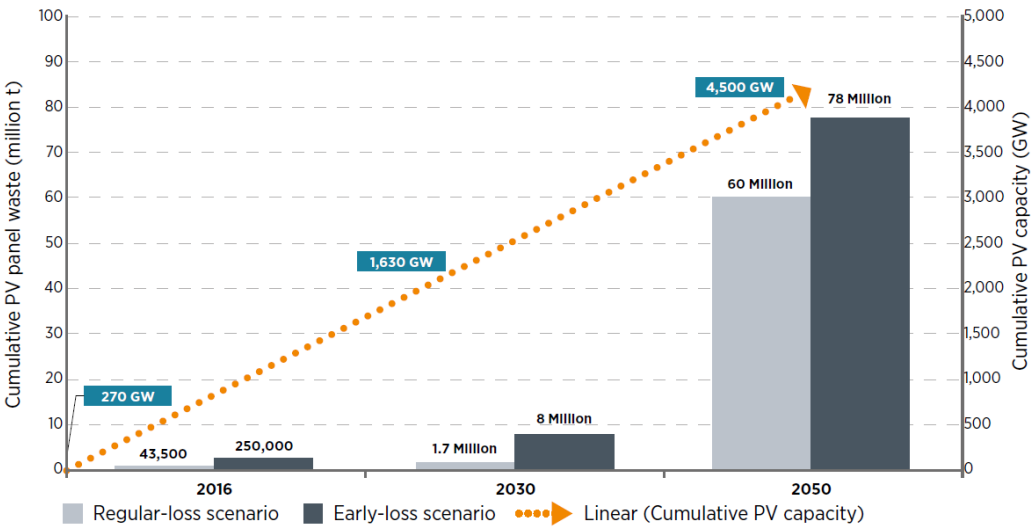
Fig. 3. Overview of global PV panel waste projections, 2016 – 2050 [1]

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In the regular-loss scenario as shown in Fig. 3 [1], PV module waste amounts to 43,500 tons by 2016 and this increases to 1.7 million tons by 2030. The early-loss scenario projection estimates much higher total PV waste streams with 250,000 tons by 2016. The early-loss scenario assumes a higher percentage of early PV module failure than the regular-loss scenario. By 2030, the top three countries for cumulative PV waste are projected to include China, Germany, and Japan as shown in Fig. 4. China is still forecast to have accumulated the greatest amount of waste, but Germany is overtaken by the United States of America at the end of 2050. The main worry is that if these solar modules are not properly recycled, they are going to contribute to world's waste and pollution levels at the end of their lives.
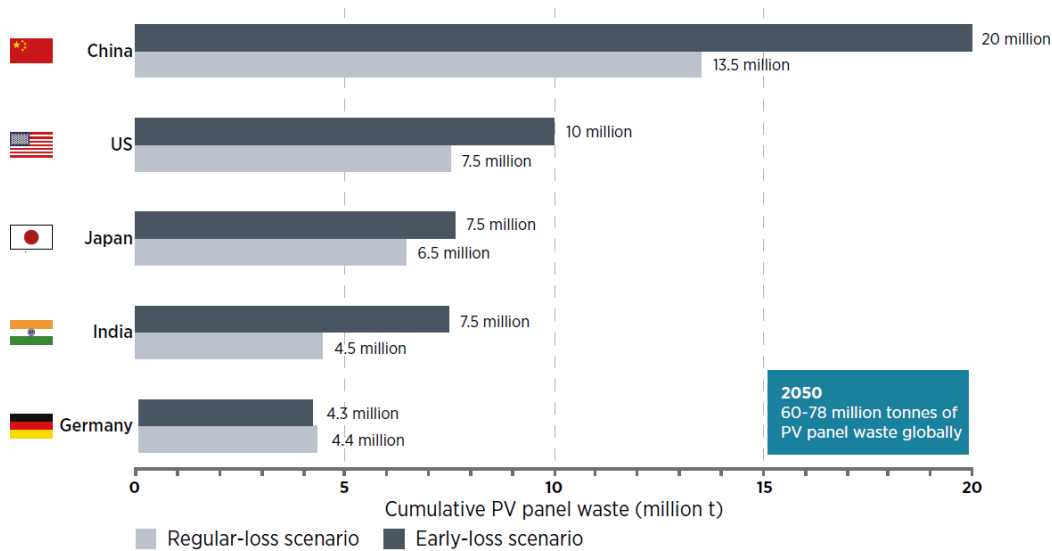
Fig. 4. Cumulative waste volumes of top five countries for the end-of-life PV modules in 2050 [1]

When a PV manufacturing facility has an annual production volume of 2000 ton of PV modules, from this tonnage only about 0.1% semiconductor material and the rest is mainly glass [6]. The total scrap amounts to nearly 200 ton for the first six months and about 100 ton/year for the rest of the facility operation. 30 years later, 2000 ton of modules per year will have to be decommissioned.

The PV modules are either classified as general or industrial waste. Large stock of raw materials can be retrieved if the PV modules are recycled at the end-of-life. By 2030, the raw materials recovered from PV modules could yield a value up to 450 million dollars as shown in Fig. 5. This is almost equal to the amount of raw materials currently required for 18 GW of power-generation capacity [1]. The recoverable value of raw materials could exceed 15 billion dollars by 2050 as shown in Fig. 5.
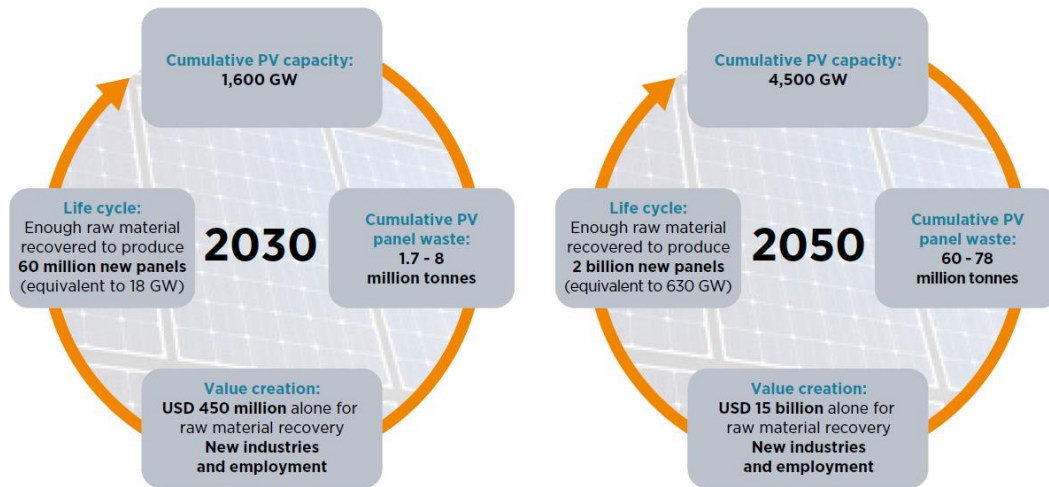
Fig. 5. Potential value creation through PV end-of-life management [1]

2.2 Potential Hazards of PV Modules at End-of-Life and Waste Characterization Tests

The end-of-life PV modules could generate toxic elements, if not properly recycled. Under normal operating conditions, PV modules pose no health or environmental hazards, as the hazardous materials, if any, used in the manufacture of PV modules are sandwiched between the layers of glass and backsheet or glass. Toxic legacy will be left by the broken PV modules as these hazardous materials, if any, are exposed and they end up in landfills where the toxic materials could leach to the ground and could affect the local water and groundwater making it not suitable for use [7]. Broken modules refer to the modules where the front glass is shattered which may result from extreme weather or human factors. Over one-third of the breakage of glass is during installation or shipping as shown in Fig. 6 which are not installed in the field. After breakage of glass in the modules during field operation, leaching to toxic metals could take place due to precipitation when landfilled and these toxic metals could be exposed to soil, groundwater, and air [8].
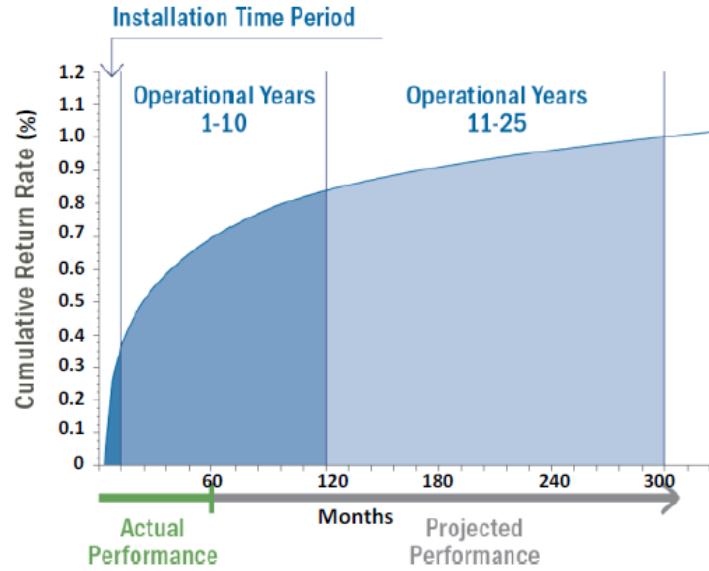
Fig. 6. Cumulative breakage rate as function of months in service [8]

In the manufacture of PV modules, lead could be used in solar PV circuits. When lead accumulates in landfills, end-of-life PV modules have the potential to leach into drinking water, as lead is highly toxic to the central nervous system of human body. In European countries and Japan, there are current regulations to use lead-free solders but in the United States, there are no such regulations. The other significant toxic elements that could be present in the PV modules are chromium and cadmium. There are also other substances which have the potential to leach from PV modules, cadmium and lead pose the largest environmental and health risks [9]. Lead could be the main toxic element found in crystalline silicon modules. High lead leaching occurs at low pH conditions, with substantially increasing the leaching in weather impacted or crushed PV modules that are exposed to low pH water.

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When the broken modules are landfilled, toxic elements could leach into the ground. Cadmium could be the main toxic element present in cadmium telluride (CdTe) modules [10]. For crystalline silicon modules, lead could be of primary concern. The Resource Conservation and Recovery Act (RCRA) regulates hazardous waste in the United States and is enforced by EPA. The TCLP testing regulated by EPA 1311 is used to determine whether specific PV modules qualify as universal waste and can be disposed in regular landfills or if they qualify as hazardous waste [2].

The concentration of certain substances in the liquid which has been exposed to fragments of broken PV modules for a defined period of time in a particular ratio is the key criterion for determining the waste classification [1]. Different leaching test methods provide different threshold values for allowable leachate concentrations for a waste material to be characterized as non-hazardous waste. These waste characterization tests are found to be more aggressive than PV field breakage conditions with regards to parameters like sample size, treatment method and solvent. In all the above three methods, testing consists of acid digestion followed by spectrometry. The summary of waste characterization leaching test methods for US, Germany and Japan are shown in Table 1 [8].

Table 1: PV waste characterization: Leaching methods in US, Germany, and Japan [8]

	US	Germany	Japan
Leaching test	US Environment Protection Agency method 1311 (TCLP)	DIN EN German Institute for Standardization standard 12457-4:01-03	Ministry of Environment Notice 13/JIS K0102:2013 method (JLT-13)
Sample size (cm)	1	1	0.5
Solvent	Sodium Acetate/acetic acid	Distilled Water	Distilled water
Liquid : Solid ratio for leaching test	20:1	10:1	10:1
Treatment Method	End-over-end agitation (30±2 rotations per minute)	End-over-end agitation (5 rotations per minute)	End-over-end agitation (200 rotations per minute)
Test temperature	23±2 °C	20 °C	20 °C
Agitation Duration	18±2 hours	24 hours	6 hours

2.3 PV Recycling Regulations

2.3.1 USA

Currently in the United States, there are no federal regulations on how to recycle the end-of-life PV modules. The end-of-life disposal is based on the federal Resource Conservation and Recovery Act (RCRA) and on state policies like California's Hazardous Waste Control Law (HWCL) [7]. If the PV modules are classified as hazardous waste by EPA 1311 Toxicity Characteristic Leaching Procedure (TCLP), RCRA is used to regulate the handling of PV modules, recycling, reuse, storage, and disposal [11]. Defective PV modules are currently considered as hazardous waste by regulators if they do not meet the U.S. Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) standards.

According to the Senate Bill 489 which was proposed in California's 2014-2015 legislative session, the end-of-life PV modules are identified as universal waste instead of hazardous waste [4]. First Solar recycles their own cadmium telluride (CdTe) modules. In July 2017, the state of Washington passed the Senate Bill 5939, which modifies state renewable energy system tax incentives and requires a takeback and recycling program for end-of-life PV modules. This law requires manufacturers to prepare stewardship plans that describe how they will finance the takeback and recycling program and provide for takeback of PV modules. Manufacturers who do not provide a recycling program cannot sell solar modules after January 1, 2021 in the United States. Solar Energy Industries Association (SEIA)

connect members to pre-approved PV recyclers, facilitate a single point of contact, and collect data on industry level recycling [11].

2.3.2 European Countries

In early 2003, the E.U established the WEEE (Waste Electrical and Electronic Equipment) and RoHS (Restriction of Hazardous Substances) directives. The minimum recycling targets with which member statistics must comply is set by WEEE [7]. Member countries include UK, Netherlands, France, Czech Republic, Germany, Spain, Switzerland, Belgium, and Bulgaria. The WEEE deals with waste, while RoHS restricts the use of hazardous substances used in the manufacture of PV modules. The European Photovoltaic Industry Association and German Business Association have launched the "PV cycle" program to develop a European-wide collection, recycling, and recovery system The PV cycle is currently headquartered in Brussels. This is an excellent first step in minimizing the end-of-life impacts of PC modules and will preclude the specific inclusion of solar PV systems in the WEEE. The PV module recycling was first mandated in 2012 through the WEEE directive [4].

The manufacturer is financially responsible for collecting and recycling PV modules, and the collection of PV modules from the customer has to be free of charge [11]. This includes the recovery, collection, and recycling targets for waste from PV modules. These initiatives aim to decrease recycling costs and increase the potential revenue streams from secondary raw materials recovered through the recycling process. The RoHS required that the solar modules sold in the E.U. market should contain only minimal amounts of lead, mercury, cadmium, chromium, polybrominated biphenyls (PBBs). The PV modules in the WEEE

directive reduces the potential negative environmental impacts of improper disposal and generates economic benefits. Limiting the quantity of PV modules improperly disposed of has positive environmental impacts of avoiding potential lead and cadmium leaching. Additionally, it avoids potential resource loss due to non-recovery of valuable conventional resources and rare metals in photovoltaic modules which are improperly disposed of.

2.3.3 Japan

The Environmental Impact Assessment (EIA) and Waste Disposal and Public Cleansing Law (Waste Law) plays an important role in the end-of-life PV modules [8]. Japan's Ministry of Environment has authority over the national waste management law. Japan's waste management law includes emission control, waste treatment, installation of recycling and waste treatment plans, waste treatment contractor management. E-waste management law in Japan was developed to handle waste treatment for refrigerators, air conditioners, televisions and washing machines. This law includes waste treatment, installation of recycling, emissions control and other waste treatment standards [11]. The green purchasing law requires local and national governments to purchase recycled products. Manufacturers and retailers are responsible for take-back, recycling, and reporting. The government is responsible for the collection systems as well as some of the recycling in rural areas. The customers are responsible for properly disposing the e-waste and bearing some of the cost for collection and recycling.

2.4 Current Recycling Process by Industry

There are different industries follow different recycling methods for PV modules in the United States and other countries around the world. Unlike in Japan and Europe, the United States does not a standard to recycle the PV modules.

2.4.1 German's Deutsche Solar AG

German's Deutsche Solar AG's treatment process for crystalline silicon modules has been one of the top recycling plants in the world since 2003, but has stopped due to high cost of recycling because of limited number of end-of-life PV modules [9]. The treatment and recycling process developed by this company involves the removal of plastic components of the panel by a thermal process, followed by the manual separation of remaining materials such as the solar cells, glass, and metals. Glass and metals including aluminum are fed into relevant recycling process and solar cells are re-etched to the wafer. The re-treated wafers are reprocessed as solar cells and panels.

It can be noted that this procedure provides the possibility for recovering intact wafers from panels. Glass can be recovered fully intact if the process is applied correctly. They reused the silicon granules recovered from treatment operations and sold or sent for recycling all other materials.

2.4.2 First Solar

Till date, First Solar recycles only Cadmium Telluride (CdTe) modules. Established in 2003, the recycling process currently operates in United States, Malaysia, and Germany.

The solar modules are first shredded and then put through a hammer mill to ensure the laminate bond is broken. Semiconductor films are removed by placing the shards of material in a rotating stainless steel with hydrogen peroxide. The glass shards are then separated from liquid portions of waste and vibrating screen is used to separate the glass from the pieces of laminate material. Glass is rinsed to remove any semiconductor material. The liquid portion of the waste is pumped into a precipitation unit and the metal compounds found in the liquid are precipitated in three stages at increasing pH. The precipitated materials are concentrated in a thickening tank for dewatering and the resulting unrefined semiconductor materials are packaged for processing for use in new solar modules. Primary raw materials recovered from semiconductor waste are Te and Cd. First Solar claims it recovers 90% of the glass used in the photovoltaic unit for usage in new glass products or in new photovoltaic modules. Since this recycling process involves using shredded photovoltaic modules, recycling broken modules, and manufacturing scrap are also feasible in this process.

2.5 Recycling Process Methods
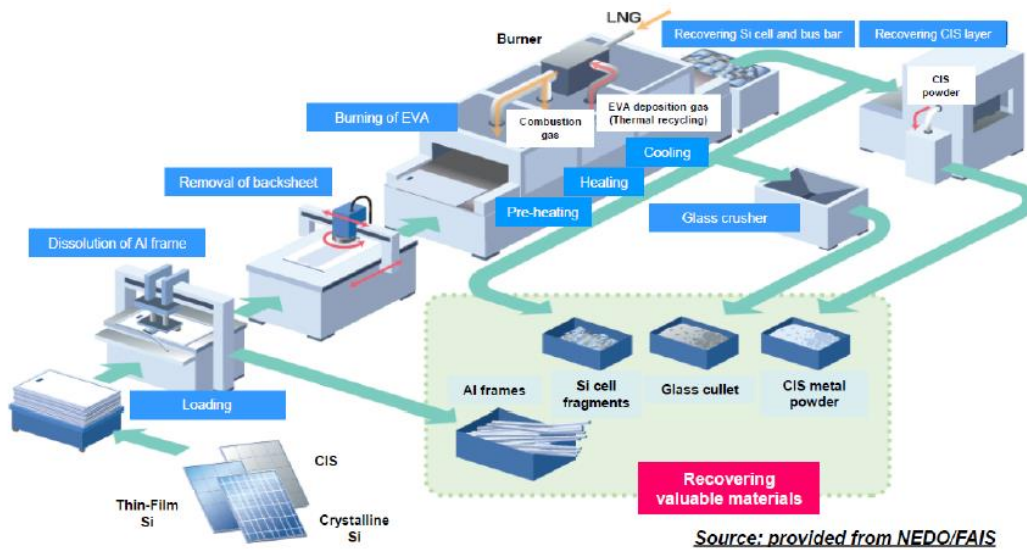
Fig. 7. Recycling Process of Japan [4]

Fig. 7 shows the recycling process (thermal and mechanical method) of Japan, first implemented by Shinryo Corporation [4]. The life of PV modules must be safe and sustainable from cradle-to-grave. Sustainability is defined by 3R's of waste hierarchy: Reduce, Reuse and Recycle [11]. Research and development in the manufacturing will help reduce the use of raw materials, especially the used of hazardous materials in the PV module lifecycle. Fig. 8 shows the process flow diagram of the life cycle stages for PV modules and resulting opportunities for reduce, reuse and recycle [1].

Modules which are operating at 80% of their power rating are usually discarded after 25 years. The glass and the frames from these degraded modules can be separated and reused after separating them from either chemical, thermal or mechanical methods. Table 2 shows

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different types of treatment for recycling of PV modules [4]. There are some parts of a degraded module where parts can be recycled. For example, the silicon wafers from old modules can be removed and used in new modules after removing the metallization and interconnects.
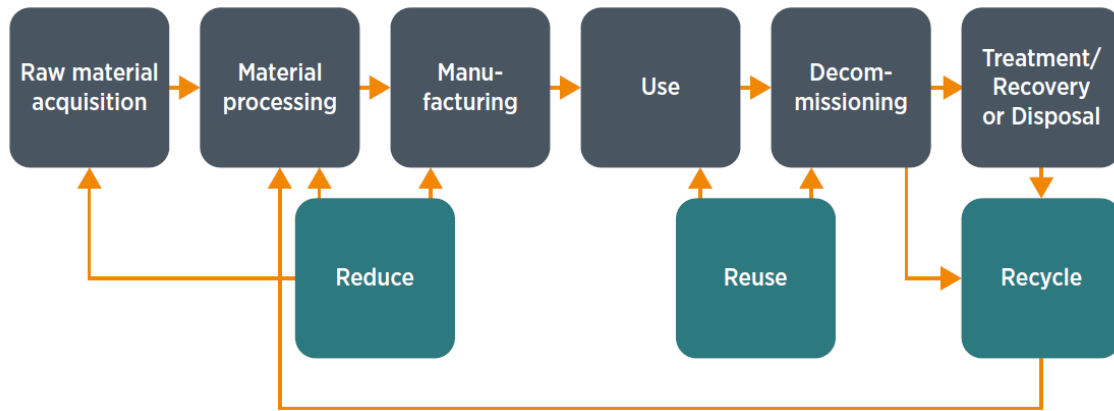
Fig. 8. Process Flow Diagram for the life cycle stages for PV modules [1]

Table 2: Basic Operations for treating and recycling PV panels [4]

Type of Treatment	Potential Treatment Steps involved
Physical/Mechanical	Crushing, Attrition, Density separation, flotation, adsorption, radiation, metal separator
Chemical	Acid/base treatment, solvent treatment
Thermal	Incineration, pyrolysis, melting, slagging
Disposal	Recycling into the same product, recovery of energy from thermal treatment of organic layers, utilization of the volume of mineral fractions, landfill cover

2.5.1 Thermal Method

Pyrolysis is one of the earliest methods used to recycle PV modules. But this method has a major drawback. This failed due to non-uniform heating temperature distribution resulting in considerable cell breakage [12]. When the modules are dissolved in a chemical reactor with tri-ethylene glycol at a temperature between 220°C and 290°C, the EVA swells up and does not release from the module. The same can be carried with nitric acid, but it is unlikely to become a viable industrial process due to large amounts of nitric acid needed. From the financial side, the thermal approach seemed to be more favorable approach than the chemical method.

Pyrolysis is carried in a conveyor belt furnace, where the EVA is burnt away in the air atmosphere or decomposed under nitrogen. Poor mechanical yield is caused by the considerable temperature increase at the silicon surface due to exothermic reaction leading to cracks. The best and efficient industrial implementation is the pyrolysis in a fluidized bed reactor [12].

The filled fine sand in the fluidized bed reactor as shown in Fig. 9 will be in a hot boiling fluidized state due to the optimized air stream. The modules are loaded in the basket and immersed in the fluidized bed. The EVA and the backsheet of the modules are gasified and the off-gases which emerge from the reactor are passed immediately through the flame shield serving simultaneously as post-combustion and as a heat source for the reactor. The optimized process temperature is around 450°C.

0. Fluidised bed   5. Pilotburner   10. Gas-air mixture
1. Calibrated quartz sand   6. Direct combustion   11. Secondary air supply
2. Air supply   7. Combustion chamber   12. Exhaust off gases
3. Gas supply   8. Hardware being cleaned
4. Gas-air distributor   9. Process gases
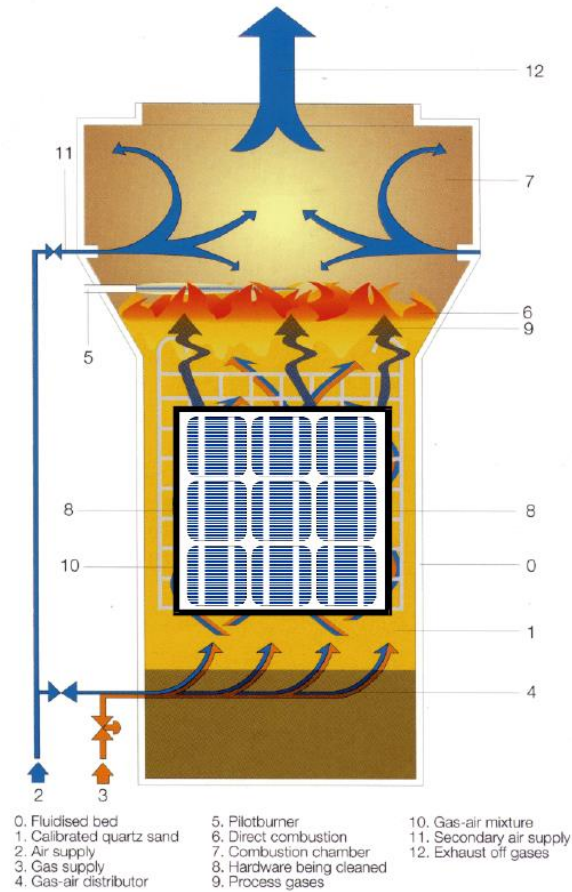
Fig. 9. Pyrolysis in a fluidized bed reactor [12]

The fluidization velocity of the fine sand particles is kept at extremely low speed (as low as 1 cm/s) for the recycling for crystalline silicon modules. The best results are yielded when the modules are placed on the basket at an angle of 60°. By this process, 100% recovery is achieved for glass sheets and 80% recovery of wafers are possible.

2.5.2 Mechanical Method

The mechanical approach for the recycling of PV modules includes crushing, scraping glass or layers, and cutting the encapsulation layers. For recovering glass, the Mitsubishi Materials Corporation mechanically scraps the cover-glass so as not to contaminate the

glass with the encapsulation (EVA) layer. The recovered glass is filtered and is assumed that transparent glass grains are provided for secondary usage. The main target element of this company is Ag because of its high value.

Pre-crushing

Manual sorting

Magnetic separator

Fine crushing

Screening — Fine grain, foil

Non ferrous separator

Extraction Unit — Foil

Color based sorting

Automatic sampling

Glass Cullet
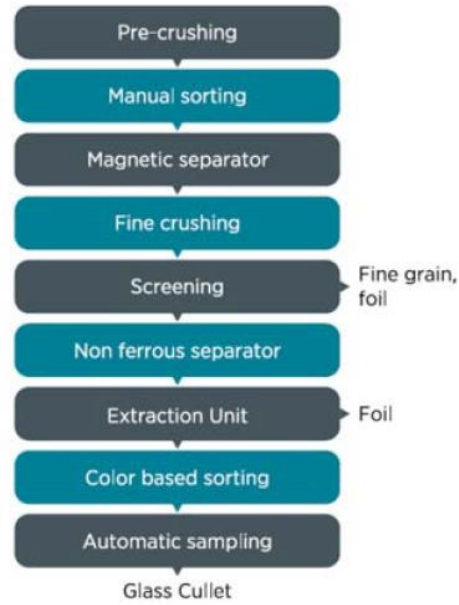
Fig. 10. Example of the process of laminated glass recycling [1]

In most of the mechanical recycling plants, the aluminum frame is first removed by non-ferrous metal separators after initial crushing or shredding as shown in Fig. 10. The aluminum is sold separately for reuse and to other recycling plants [11]. The mixed metals which includes aluminum parts, copper interconnects, and some solar cell fragments are separated after crushing. The separation of encapsulant and backsheet materials are done by aeraulic sorting in which the compressed air is used to provide the energy for separation of glass and encapsulant materials. This output is checked for halogen content. If the halogen content is too high, then incineration in a hazardous-waste treatment plant is

carried out. Color based sorting is carried out in case to remove any impurities present. In some cases, solar cell fragments detected are blown out using compressed air. The remaining material is the glass which is pure. Fig. 11 shows the generic steps in PV recycling [11]. In the disassembly process, frames, wires, junction box are recovered. The breaking of sandwich into its components takes place in the delamination process where mainly glass and solar cells are recovered by mechanical or thermal process.
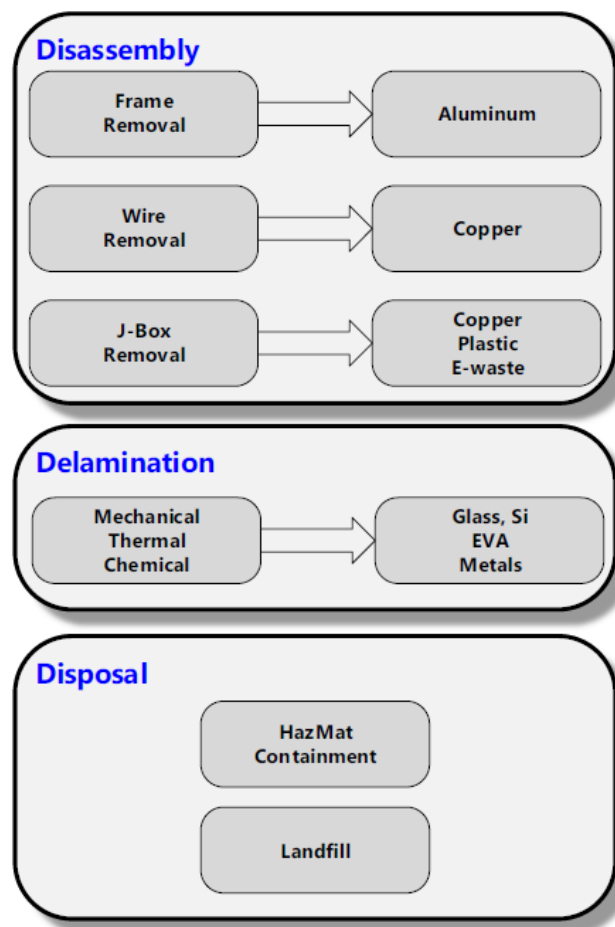
Fig. 11. Generic steps in PV Recycling [11]

Toho Kasei scrape the non-glass layers mechanically. The first two steps are to scrape the backsheet and then the EVA layer, including the solar cells and the electrodes. The encapsulation layer is then treated by solvent. The scraped backsheet is disposed of as industrial waste. Hamada Corporation have developed means of cutting the encapsulation layer alongside the cover glass using the heated cutter [4]. The laminate frame is incised by heated cutter after removing the frame with a machine and scraping the backsheet. The cutter is inserted into the bonding plane between the glass and the encapsulation layer while avoiding damage to the glass surface. The glass is recycled as a cullet after removing the encapsulation materials attached to the glass surface.

2.5.3 Chemical Method

Yokohama Oils & Fats industry developed one of the first chemical method for recycling of PV modules. Aluminum frames and junction boxes are removed from PV modules manually and the backsheet is removed mechanically. The remaining laminated structure is immersed in a neutral solvent, and glass and other layers for encapsulation (EVA), the Si cells, and the electrodes are separated. The separated glass can easily be reused or recycled. The remaining laminated structure is immersed in a neutral solvent, and glass, EVA, solar cells, and the electrodes are separated. The remaining layer is crushed and immersed in an alkali solvent. The EVA, silicon and ribbon are recovered after the immersion step. The expected processing time using chemical method is almost one day for commercial modules.

Korea Research Institute of Chemical Technology (KRICT) with Kangwon National University developed a technology for dissolving EVA by submerging modules in an

organic solvent and using additional ultrasonic irradiation. The ultrasonic irradiation is used to overcome the shortcomings of chemical separation, which requires a long treatment time [4]. An additional process for recovering metals from Si cells will be required after eliminating the encapsulant from the laminated structure. Some technologies rely on acid and alkali hydroxide for chemical etching. Loser Chemie developed a technology which uses aluminum chloride and water. Aluminum electrodes on the backsides of Si cells can be recovered with poly-aluminum-chloride, which is a valuable product for the treatment of wastewater.

3. METHODOLOGY

3.1 TCLP Testing

To identify potential sources of variation in TCLP results due to module sampling and preparation methods, the toxicity testing done by the two TCLP labs are analyzed. The samples which were removed from the PV modules from various sampling methods are sent to the two TCLP labs to check for the reproducibility between the labs.

The EPA 1311 method for TCLP testing involves a module test sample to a particle size of less than 9.5 mm, adding an extraction fluid at a 20-to-1 fluid-to-sample weight ratio, and rotating the sample (agitating the sample) in the extraction fluid for 18-20 hours [2]. During agitation, leaching of toxic metals take place to the extraction fluid, and this fluid will be tested for the presence and amount of toxic elements by atomic absorption method. The standard specifies the pH of the extraction fluid to be 4.93 ± 0.05, and this pH will be maintained by the testing labs. Elements regulated by the TCLP include arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver.

Table 3 shows the detection limit of various toxic elements from lab 1 and lab 2, and Table 4 shows the summary of test procedures of the two TCLP laboratories.

Table 3: Detection limit (DL) of Toxic metals for the two TCLP laboratories

Metal	Lab 1 DL (mg/l)	Lab 2 DL (mg/l)
Mercury	0.01	0.001
Arsenic	0.1	0.4
Barium	0.1	0.5
Cadmium	0.1	0.02
Chromium	0.1	0.3
Lead	0.1	0.4
Selenium	0.1	0.4
Silver	0.1	0.1

Table 4: Summary of test procedures of the two TCLP laboratories

Factors	Lab 1	Lab 2
Detection Method	Atomic Absorption Method	Atomic Absorption Method
Sample Size	< 9.5 mm	< 9.5 mm
Solvent [Water : NaOH : Acetic Acid Ratio]	1 : 0.01605 : 0.00855	1 : 0.01356 : 0.006
Liquid : Solid Weight Ratio	20:1	20:1
Agitation Time	18±2 hours	19 hours
Agitation rpm	30±2 rpm	30 rpm (custom made agitator)
Test Temperature	23±2 °C	23 °C

3.2 Modules for Sample Removal

For the TCLP testing, samples have to be removed from the different areas of the laminate. Five module manufacturers were selected randomly for sample removal from the laminate area to determine the amount of toxicity in the modules. Table 5 shows five different module manufacturers used for laminate sample removal along with some of the specifications.

Table 5: Specifications of different modules used for sample removal

	Weight (kg)	Length (mm)	Width (mm)	No. of cells	Technology
Module A	18.6	1650	992	60	Poly-Si
Module B	18.4	1650	992	60	Poly-Si
Module C	19.1	1650	990	60	Poly-Si
Module D	20	1635	982	60	Poly-Si
Module E	17	1575	825	72	Mono-Si

3.3 Determining Individual Weights of a PV Module

There are three main parts in a PV module: laminate, frame and junction box, cables and connectors (JCC). The PV laminate includes all the cell areas (layers of glass, front-cell encapsulant, cells with cell-interconnects, back-cell encapsulant and backsheet), the non-cell areas (layers of glass, encapsulant, backsheet) and the string-ribbon areas. The frame is usually made of aluminum and is stuck to the laminate by silicone sealant on the edges of the laminate. The junction box is stuck to the backsheet of the laminate using silicone sealant. The string ribbons from the module are connected to the junction box. The individual weights of laminate, frame and JCC are determined as follows:

3.3.1 Laminate

The entire module is first entirely cleaned to remove any dirt and soiling. To measure the weight of the entire laminate area of a module, first the entire weight of the module is measured using a spring balance (W_1 – kg). The entire length (L_1 – mm) and the width (L_2 – mm) of the module is also measured. Weighing only the laminate of the module is the most accurate way but not simpler, as it is difficult to separate the frame from the laminate. A small aluminum tray is first weighed and is kept beneath the area where a small piece of the laminate of known dimensions is cut using a diamond turbo cutting blade of 4-½" diameter as shown in Fig. 12. The use of aluminum tray is to collect any kerf particles while cutting the laminate. The cut laminate piece is kept inside the aluminum tray and weighed. Subtracting this weight with the lone weight of the aluminum tray gives the weight of the laminate piece cut.
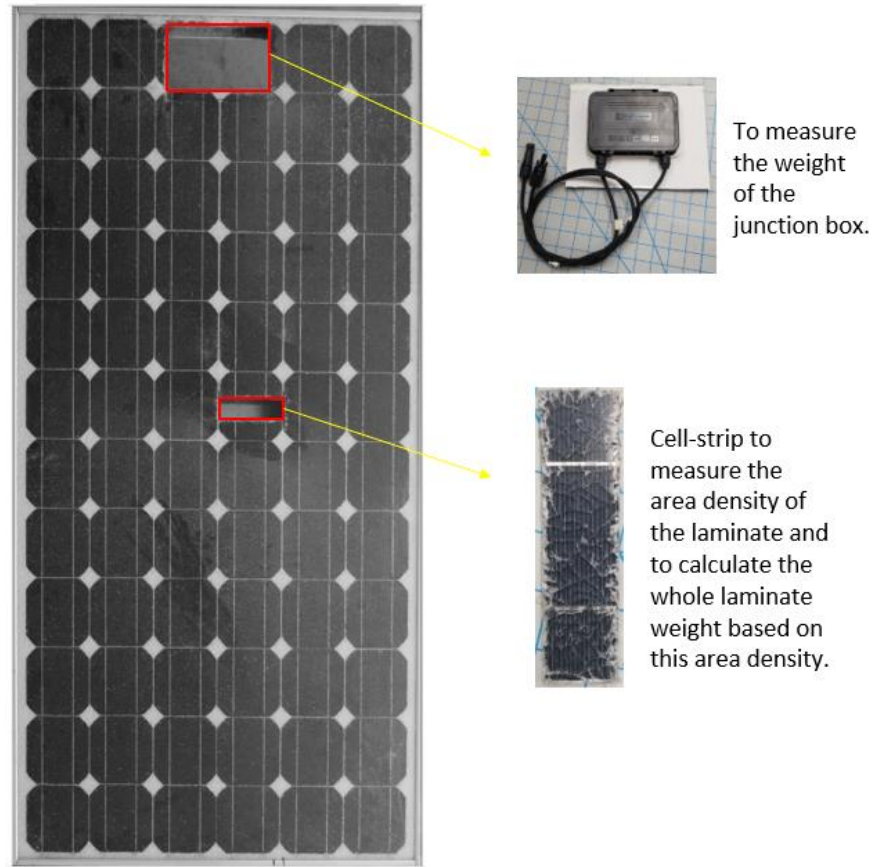
Fig. 12. Module showing a laminate piece cut to calculate the area density of the laminate

To calculate the area density of the laminate, the area of the gap in the module where the laminate piece was cut, is measured. This gives an accurate estimation of the area density $(d_1 - kg/mm^2)$ of the laminate, which is the ratio of the weight of the laminate piece cut to the area of the gap in the laminate. A small amount of laminate area will be hidden under the frame for any module. The length from the hidden edge of the laminate to the outer edge of the frame is called the groove thickness. The groove thickness $(L_3 - mm)$ is

measured by cutting a small amount of the frame using a metal cut-off cutting wheel. The total area of the laminate of the module can be calculated using the equation (1).

$$a_1 = [L_1 - (2 * L_3)] * [L_2 - (2 * L_3)] \qquad ......(1)$$

The total weight of the laminate (W_2 – kg) can be calculated by the product of the area density (d_1 – kg/mm^2) and the total area of the laminate (a_1 – mm^2).

3.3.2 Junction box, Cables, and Connectors (JCC)

To measure the weight of JCC, known dimension of the laminate is cut above the JCC using a diamond turbo cutting blade of 4 ½" diameter as shown in Fig. 12. Then the area of the laminate above the JCC (c_1 – mm^2) and the total weight of the laminate cut and JCC (W_3 – kg) are measured. The combined weight of the junction box, cables, and connectors (W_4 – kg) is calculated using the equation (2) as the area density of the laminate is known.

$$W_4 = W_3 - \left[c_1 * \left(\frac{W_2}{a_1}\right)\right] \qquad ......(2)$$

3.3.3 Frame

Since the total weight of the module and the weights of laminate and junction box, cables, and connectors (JCC) are known, the weight of the frame (W5 – kg) can be calculated using the equation (3).

$$W_5 = W_1 - (W_2 + W_4) \qquad ......(3)$$

Measure the entire module weight [W_1 – Kg]

Calculate the density of the laminate by cutting a small piece of the laminate [d_1 – Kg/mm²]

Measure the total area of the laminate considering the groove thickness also [a_1 – mm²]

Calculate the weight of the laminate
[$W_2 = d_1 \times a_1$ Kg]

Measure the area of the laminate above the junction box cut [c_1 – mm²]

Total combined weight of the junction box and the laminate cut [W_3 – Kg]

Calculate the weight of the junction box
[$W_4 = W_3 - (c_1 \times W_2 / a_1)$ Kg]

Calculate the weight of the frame
[$W_5 = W_1 - (W_2 + W_4)$ Kg]

Fig. 13. Flowchart to calculate the weight of individual parts of the module

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3.4 Determining Individual Areas of the Laminate in a PV Module
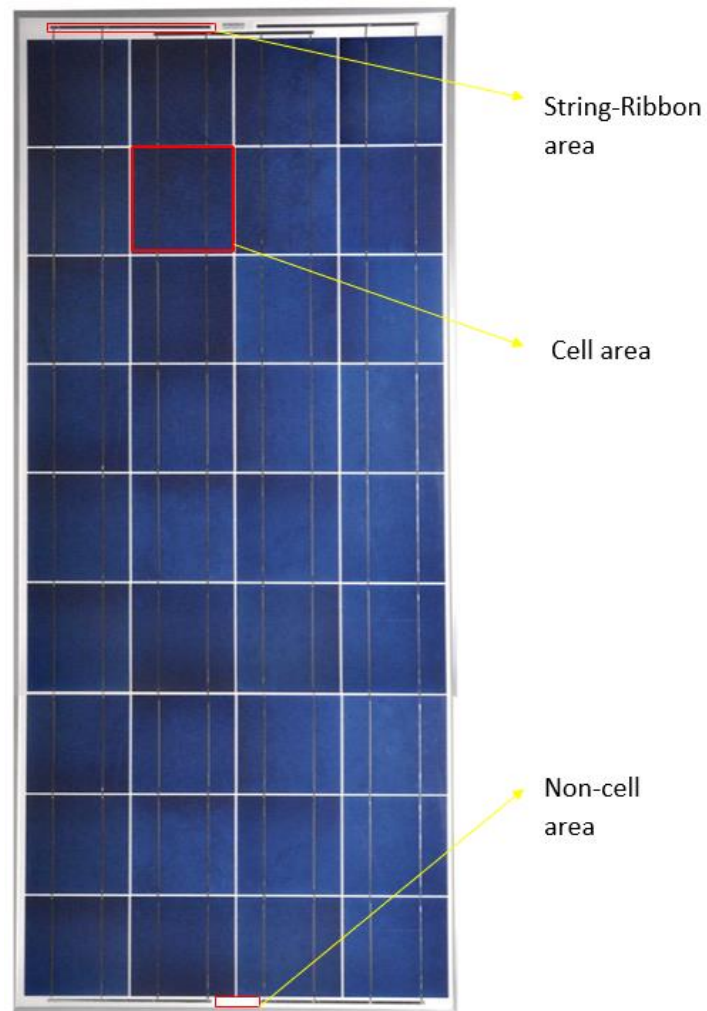
Fig. 14. A module showing different areas of the laminate

The TCLP labs require only 100-110g of laminate samples with size less than 9.5mm. To avoid biased results and to meet TCLP labs' weight restriction, it is imperative that the samples of the laminate are proportionally removed from three distinct area categories as shown in Fig. 14: cell area, non-cell area, and string-ribbon area. The cell area materials

include the cell-interconnects (a potential source of lead), metalized finger contacts and semiconductor materials, and the non-cell polymeric and glass materials below and above the cells. The non-cell areas include intercell dead areas, the areas between the outer-cells' edges and laminate edges. The string-ribbon areas include the string-ribbons, glass, encapsulant, and backsheet.

To calculate the cell area, first the number of cells (n) in the module is calculated. Then the area of one cell (a_2 – mm^2) is calculated, and the whole cell area (a_3 – mm^2) which is basically the product of the area of one cell and the number of cells. The string-ribbon area is the ribbon area on the sides of the module which usually runs parallel to the width of the module as shown in Fig. 14. The area of string-ribbon (a_4 – mm^2) is calculated by measuring its length and width. In some cases, the string-ribbon will be sandwiched between two layers of the backsheet and it will not be visible from the glass side nor from the backsheet side. To find the length and width of the hidden string-ribbon, the layer of the backsheet where the hidden string-ribbon is located, is removed by using a Dremel tool as shown in Fig. 15. The tip used in the Dremel tool is the sanding bit which grinds the surface. After removing a layer of the backsheet and the glass side of the module is kept in front of a powerful light source (preferably sun), the string-ribbon will be visible from the backsheet side. Then the length and width of the string-ribbon are measured.

Fig. 15. Dremel tool to remove the layer of backsheet

The non-cell area is basically the area of the laminate where there are neither cells nor string-ribbons. The non-cell area (a_5 – mm^2) is calculated by subtracting the cell area and the string-ribbon area from the whole laminate area. The proportional different areas of the laminate are calculated using the equations (4), (5) and (6).

$$Cell\ area\ in\ \%\ proportion = \left(\frac{a_3}{a_1}\right) * 100\ \% \qquad \qquad ......(4)$$

$$Non-cell\ area\ in\ \%\ proportion = \left(\frac{a_5}{a_1}\right) * 100\ \% \qquad \qquad ......(5)$$

$$String-ribbon\ area\ in\ \%\ proportion = \left(\frac{a_4}{a_1}\right) * 100\ \% \qquad ......(6)$$

3.5 Sample Removal Methods

To supply test samples (or particles) to TCLP labs, four different sample removal methods have been applied to the PV module laminate, excluding the frame, junction box, cables, and connectors: i) coring approach, ii) cell-cut approach, iii) strip-cut approach, and iv) hybrid (combination of coring and strip-cut) approach. The removed test samples were sent to two TCLP testing labs. The PV laminate includes all the cell areas (glass, front-cell encapsulant, cells with cell-interconnects, back-cell encapsulant and backsheet), the non-cell areas (glass, encapsulant, backsheet, and string-interconnects) and the string-ribbon areas. Like earlier discussed in the introduction, the frame and junction box, cables and connectors (JCC) are recyclable and reusable materials, but if they are scheduled to be landfilled, the weight and test results of the cored/removed samples from these components shall also be included in the calculations. Most importantly, the presence of toxic metals in these parts are very minimal or zero, and sometimes not detected by the TCLP testing laboratories.

3.5.1 Coring Approach

Fig. 16. CRL AMZ1 Diamond Drilling Machine

Before removing samples from the laminate, the laminate is thoroughly cleaned with water

to remove any soiling and with isopropyl alcohol to remove organic impurities, if any. For

the coring approach, a diamond coring bit is used to remove samples from the laminate.

The CRL AMZ1 Production Diamond Drilling Machine as shown in Fig. 16 is used for

coring which has a ¼ H.P. DC Motor which has a maximum 2900 rpm [3]. The temperature

during coring process is kept near the room temperature and this is assured by constantly

cooling using distilled water. Per Method 1311 of EPA, the sample size can be a maximum

of 9.5 mm. So, a ½ inch Belgian thread and the inner diameter of 9.5 mm was used.
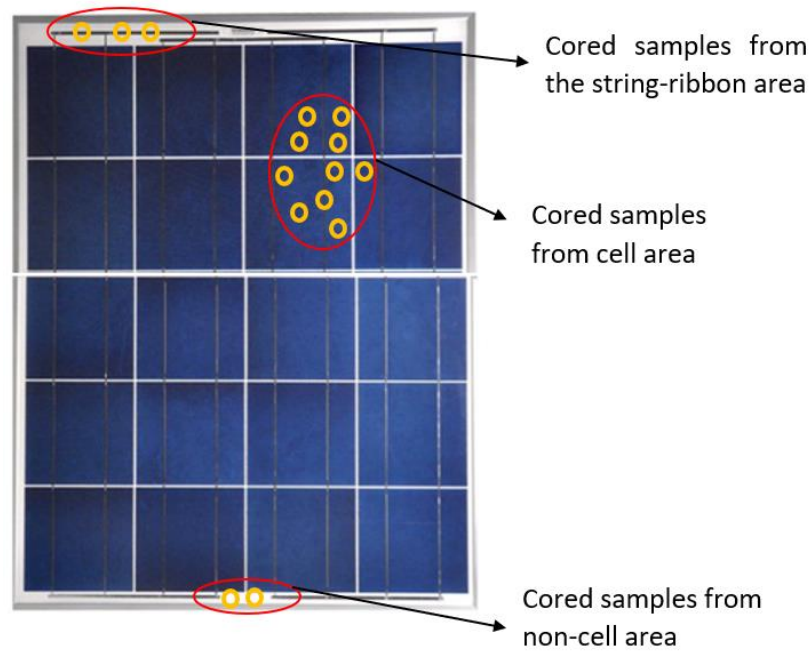
Fig. 17. A PV module showing different sample removal areas of the laminate for Coring approach

The number of pieces cored from different parts of the laminate is selected such that the total sample area is proportional to the relative areas of the cell, non-cell, and string-ribbon portions of the laminate. Most of the crystalline silicon modules have tempered glass and it breaks into a large number of small harmless random pieces when cored for the first time in the module [13]. When coring was initially started on a fresh module, the tempered glass was intact without any breakage or cracks. But after several seconds, the glass pieces were shattered with a sudden burst throughout the glass surface of the entire module.
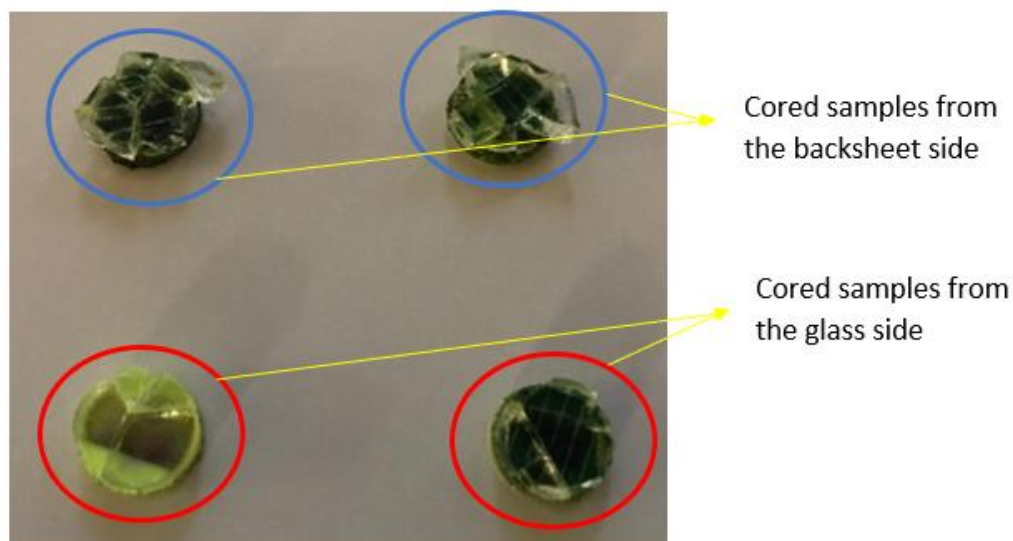
Fig. 18. Difference in the samples cored from backsheet side and glass side

Samples can be cored either from the glass side or from the backsheet. When the samples are cored from the glass side, the cored samples will mostly get stuck inside the coring bit, and the coring bit must be removed from the coring machine each time to remove the sample which is stuck in the coring bit. Also, since the glass pieces are previously shattered to pieces because of the tempered glass of the module, the glass coverage on the cored piece will not always be 100%. Sometimes significant amount of glass pieces may be broken off and dislodged from many of the cored pieces as shown in Fig. 18. In around 10% of the cored pieces, the glass pieces will be completely shattered and separated from the other layers of the laminate (EVA, cell, and backsheet). These cored pieces are not considered for TCLP testing and are discarded. The glass coverage or crack length variability depends on the interface between cell components and leaching solvent which in turn depends on the glass coverage area or crack length.
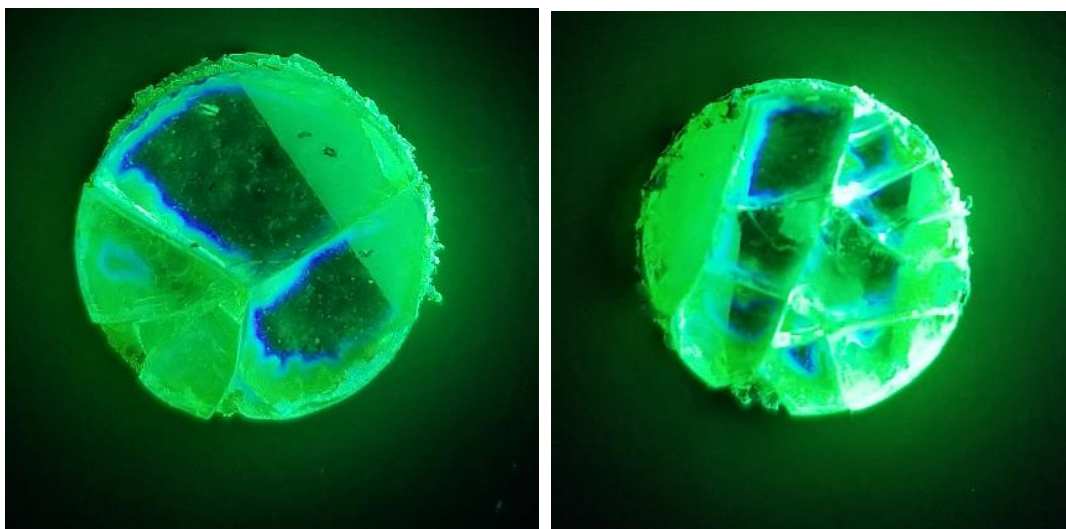
(a)　　　　　　　　　　　　*(b)*
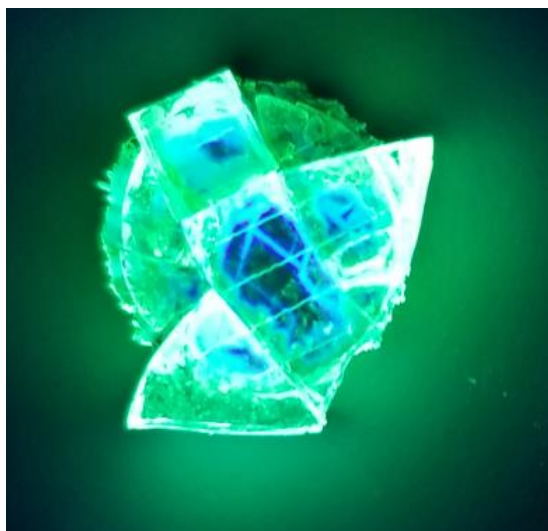
(c)

Fig. 19. (a) UV image of cored sample from the glass side which has <100% glass coverage, (b) UV image of a cored sample from the glass side which has <<100% glass coverage, (c) UV image of a cored sample from the backsheet side which had >100% glass coverage

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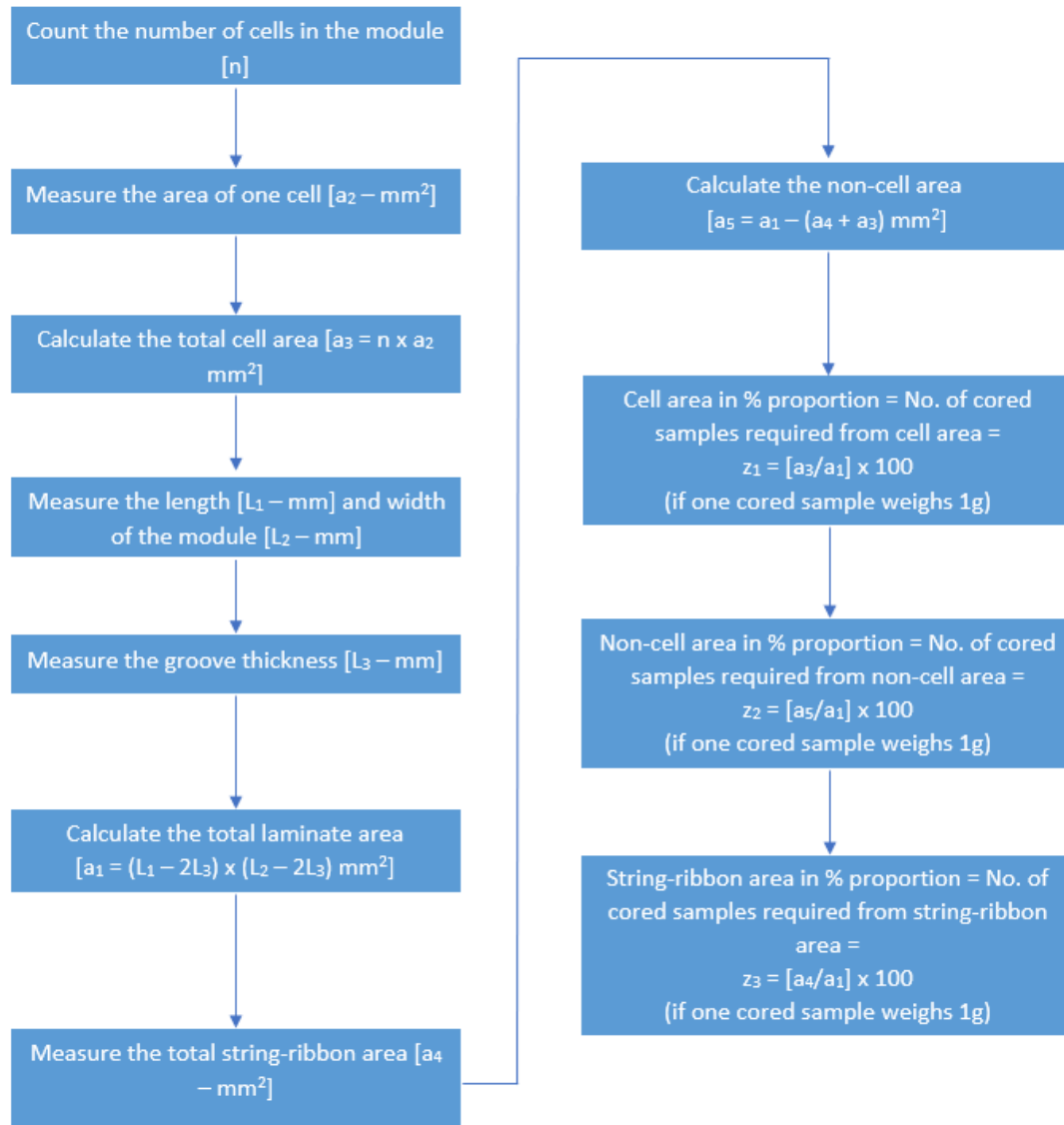
Fig. 20. Flowchart to calculate the proportional pieces to be cored from laminate for coring approach

When coring from the backsheet, the cored piece is actually pushed and falls off beneath the module and this cored piece is collected by keeping a disposable aluminum tray beneath the module. As shown in Fig. 19(c) the glass piece coverage of the cored sample will be sometimes greater than 100% as the glass layer is not entirely cored and basically pushes the coring piece instead of coring the glass layer. Thus, coring from the glass side is recommended.

To avoid biased test results, the sampling procedure implemented by this research team proportionally combines pieces coming from all the three laminate areas. Two cored laminate samples (cored from the glass side) weighing between 100 and 110g each was sent to a recognized TCLP lab. To avoid damage to the cored samples while shipping to the testing labs, the cored samples were kept in small containers and is sealed in a compact cushion shipping box. Another two cored laminate samples weighing between 100 and 110g was sent to another recognized TCLP lab and the test results from two labs were compared for reproducibility between the labs and repeatability within the labs. Clear instruction was given to both the TCLP labs not to crush the sent samples further to maintain the consistency of size 9.5 mm.
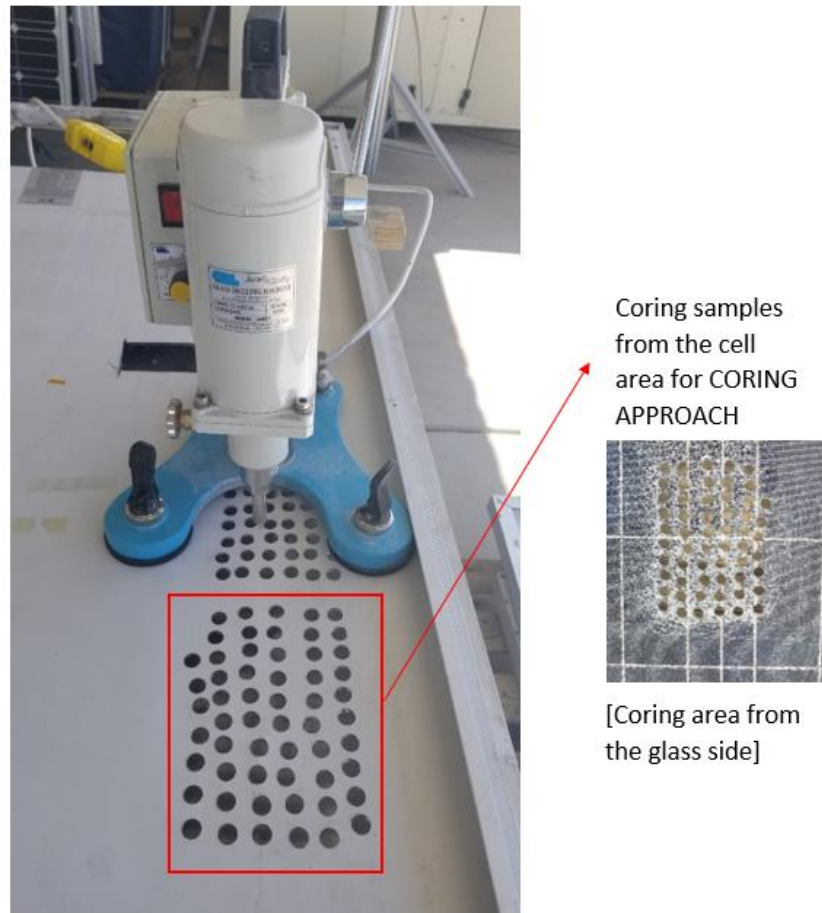
Fig. 21. A cored laminate for the coring approach with the coring machine (module shown from the backsheet side)

3.5.2 Cell-cut Approach

The coring approach takes a long time; around 3 hours to core 100-110g of sample. To reduce the time taken to remove samples from the laminate, cell-cut approach was introduced.

Fig. 22. Cutting a cell using a diamond cutting wheel

In a typical, modern PV laminate, the dimensions of each cell piece are about 16cm x 16cm, and the weight of each cell piece is about 265g - 270g. In this approach, one whole cell of a module is cut using a 4 ½" diamond cutting wheel. Two full cell pieces including glass, encapsulant, and backsheet cut from the laminate were sent to the two TCLP labs so the results obtained from the coring method and strip-cut method could be compared and this was performed twice to check for repeatability within a lab.

Fig. 23. Cell-cut piece on a weighing scale

For the first samples of cell-cut approach, the TCLP labs were not given any instruction. The two TCLP labs were given the freedom to cut small pieces from any location within the supplied full cell piece to meet their 100-110g requirement and crush the piece to meet the EPA 1311 required size of less than 9.5mm. It is possible that each TCLP lab cut the 100-110g piece from multiple different locations and orientations from the 270g full cell piece. For example, the first TCLP lab may have cut the 100-110g piece along one of the cell interconnect ribbons containing lead and the second TCLP lab may have cut the 100-110g piece along one of the cell edges completely avoiding the cell interconnects containing lead. So, the first lab would report the presence of lead whereas the second one would report the absence of lead.

Fig. 24. Image of sample 1 unused for testing from lab 1

The Fig. 24 shows the image of sample 1 which was unused for TCLP testing by Lab 1. This image clearly shows that the sample used for TCLP testing was cut by the lab parallel to the cell interconnect ribbons to meet their 100g – 110g requirement. The testing is biased by lab 1 as two cell interconnect ribbons were included in the sample tested and does not proportionally represent the whole cell. This will show a higher result of lead content. To avoid damage to the cell while shipping to the testing labs, the whole cell is carefully wrapped in thin aluminum foil and is sealed in a compact cushion shipping box.

For the second set of samples sent to the TCLP labs, clear instruction was given to cut the sample perpendicular to the cell interconnect ribbons to meet their 100g – 110g requirement for unbiased testing of the labs. The main disadvantage of this approach is that pieces from non-cell area and string-ribbon area are not removed, and the sampling includes only the cell area.

3.5.3 Strip-cut Approach

In the cell-cut approach, the testing labs will cut the sample for their required weight for testing. Although instruction was given on how to cut the sample, there will be variation in cutting from person to another. To reduce this variation, strip-cut approach is introduced.
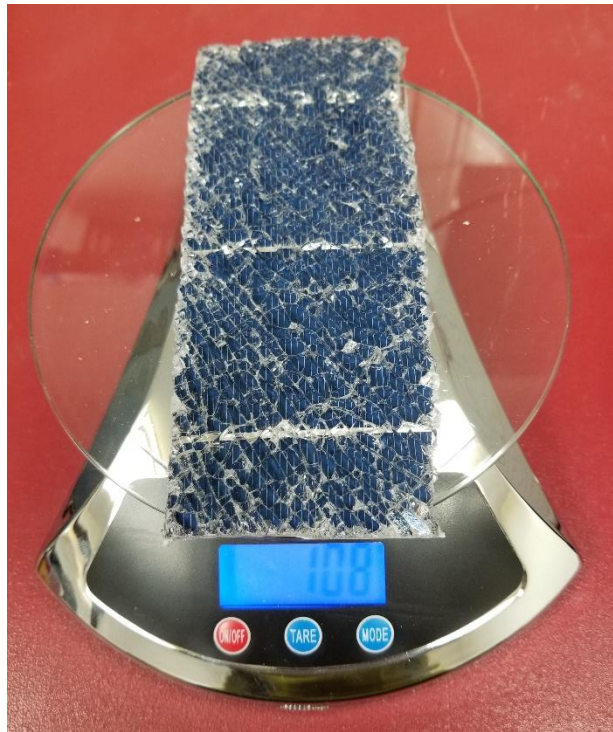
Fig. 25. Strip-cut piece on a weighing scale

Two TCLP labs were supplied with laminate strips of the required weight (100-110g) and from locations and orientations representing the entire cell. For the strip-cut approach, two strips were cut in the cell area of the laminate using a 4 ½" diamond cutting wheel such that each strip weighed between 100g and 110g, as shown in Fig. 25. The length of the cell

strip is kept constant (the length of the cell), and the width of the cell strip is selected such that the cell strip weighs between 100g and 110g based on the area density of the laminate. Each strip was cut perpendicular to the length of cell interconnect ribbons such that it was representative of the full cell, covering both the interconnect and non-interconnect regions of the cell. Two strips were sent to two TCLP labs, and the labs were given the freedom to crush the piece to meet the EPA 1311 required size of less than 9.5mm. To avoid damage to the strip while shipping to the testing labs, the sample strip is carefully wrapped in thin aluminum foil and is sealed in a compact cushion shipping box.

3.5.4 Hybrid Approach
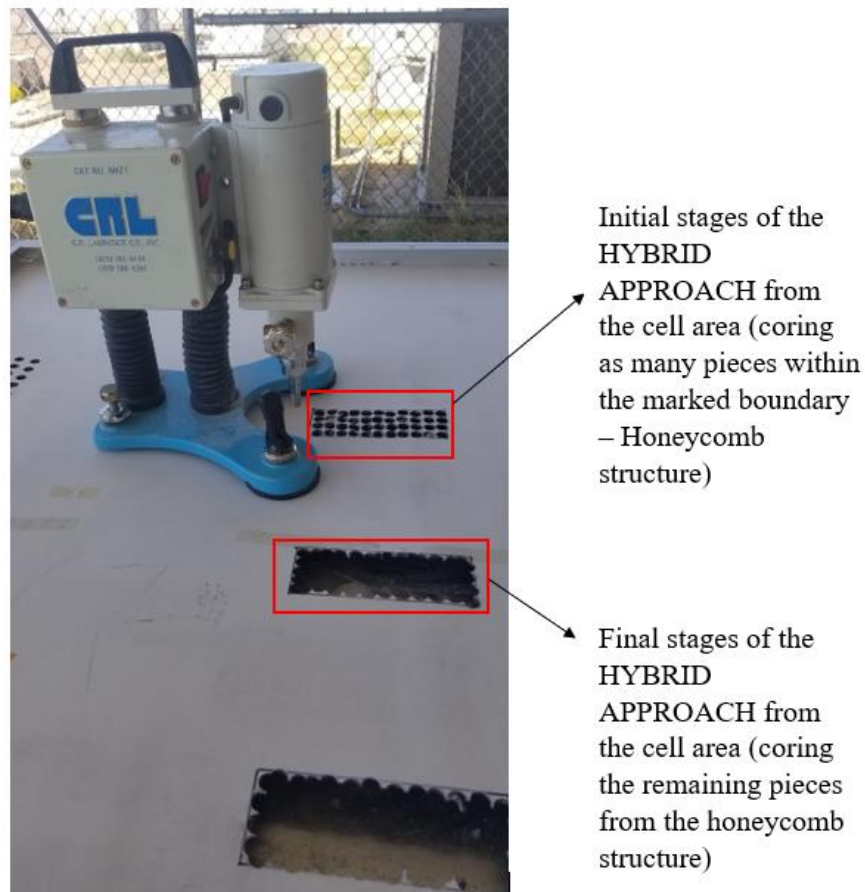
Fig. 26. Stages of Hybrid approach from the cell area (shown from the backsheet side of the PV module)

In the strip-cut approach, the TCLP labs have to reduce the sample size to less than 9.5mm. The EPA 1311 standard only says the maximum size of the sample but not the minimum size. In this case, the labs may reduce to sample to exactly 9.5 mm or crush the samples to micron level. The same applies to cell-cut approach also. The variability in the sample size

will be high and is unknown how the testing labs reduce the sample. To reduce this variability in sample size, Hybrid approach is introduced.
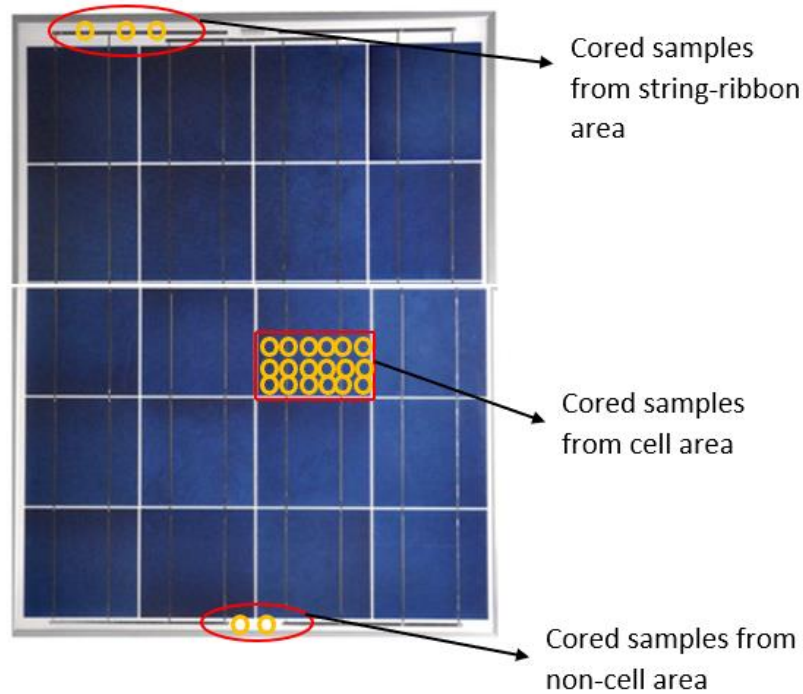
Fig. 27. A PV module showing different sample removal areas of the laminate for Hybrid approach

The hybrid-cut approach is basically a combination of the strip-cut and coring approaches. All the three main areas (cell, non-cell, and string-ribbon) of the laminate are considered in this approach as in the coring approach. To remove samples from the cell area, the strip-cut approach is followed. Keeping the length of the cell strip constant (the length of a cell), the width of the cell strip is selected such that the sum of the weight of the cell strip and the proportional number of pieces in terms of area which will be cored from the non-cell and string-ribbon area falls in-between 100g and 110g. Cutting the cell strip and then coring

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on the strip was challenging. In this case, a boundary of the strip is first marked in the cell area. Then a disposable lightweight aluminum tray is kept beneath this area to collect any kerf particles while coring from the glass side.

As many pieces are cored (coring is done as close to each other and the size of 9.5 mm is maintained) within this marked boundary of size 9.5mm as shown in Fig. 26 (a honeycomb structure will be formed). Then the remaining pieces from the honeycomb structure are also cored, but the sample pieces will not be of size 9.5 mm but less than 9.5 mm. Since these pieces are of size less than 9.5 mm, the samples will not get stuck inside the coring bit and falls off on the aluminum tray and is not required to remove the coring bit each time after coring one sample. This reduces the overall time consumed to remove samples when compared to the coring approach (coring from the glass side).

To represent the non-cell area and ribbon area of the laminate, the coring approach is followed where proportional pieces are cored in the non-cell and string-ribbon areas using the ½' diamond coring bit. The cored strip of the cell area (along with the kerf loss), cored non-cell and string-ribbon samples represent the whole of the laminate area, proportionally.

Count the number of cells in the module [n]

Measure the area of one cell [a_2 – mm²]

Calculate the total cell area [a_3 = n x a_2 mm²]

Measure the length [L_1 – mm] and width of the module [L_2 – mm]

Measure the groove thickness [L_3 – mm]

Calculate the total laminate area [a_1 = (L_1 – $2L_3$) x (L_2 – $2L_3$) mm²]

Measure the total string-ribbon area [a_4 – mm²]

Calculate the non-cell area [a_5 = a_1 – (a_4 + a_3) mm²]

Cell area in % proportion = z_1 = [a_3/a_1] x 100

Non-cell area in % proportion z_2 = [a_5/a_1] x 100

String-ribbon area in % proportion z_3 = [a_4/a_1] x 100

- Measure the length [L_4 – mm] and width [L_5 – mm] of the cell area strip.
- Calculate the area of the strip [a_6 = L_4 x L_5 mm²]

Calculate the area of one cored sample [a_7 = π/4 x 9.5 x 9.5 = 70.88 mm²]

- Area of non-cell to be cored [a_8 = z_2 x a_6 / z_1 mm²]
- No. of cored pieces required from non-cell area = c_8 / a_7

- Area of string-ribbon to be cored [a_9 = z_3 x a_6 / z_1 mm²]
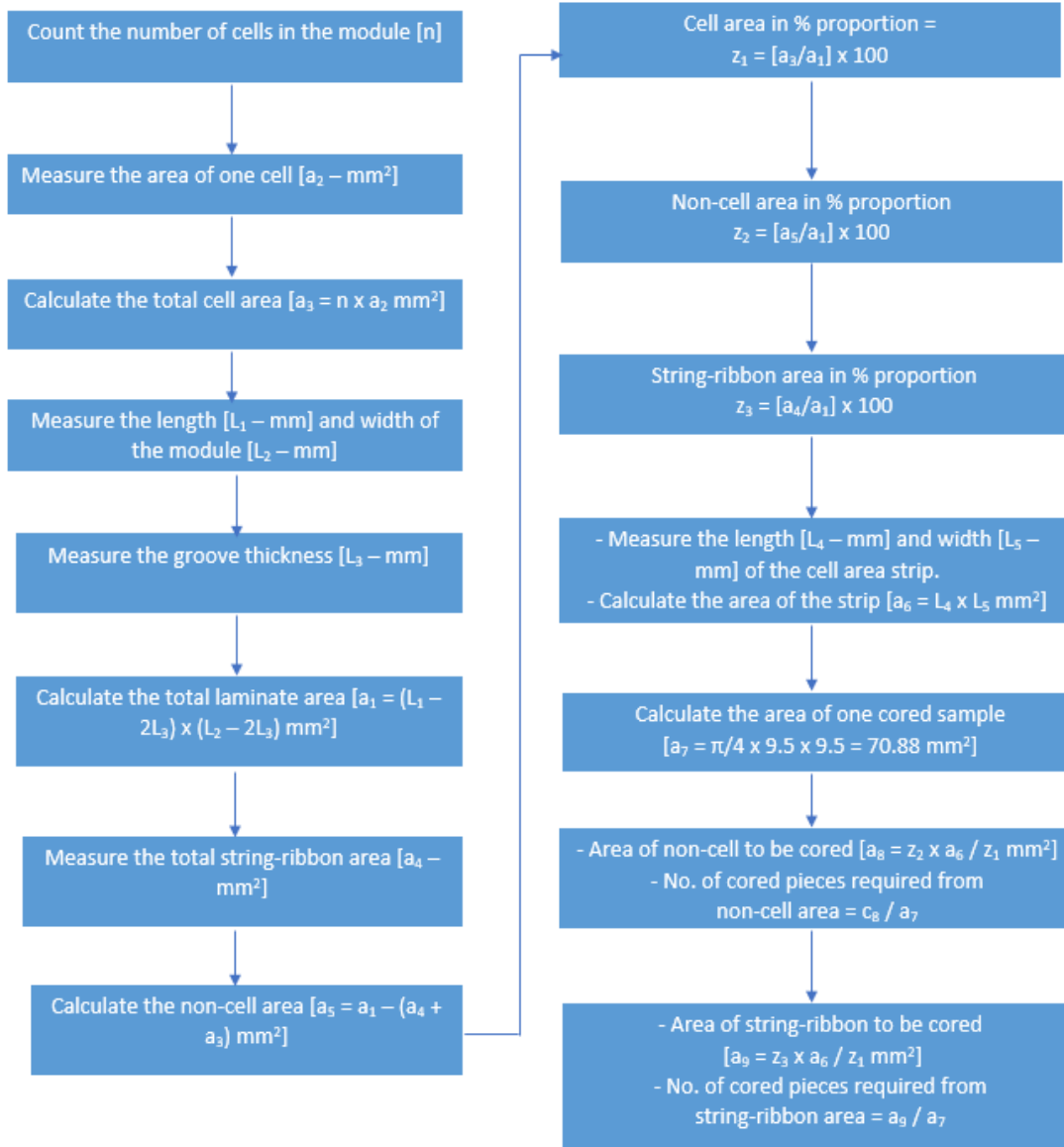- No. of cored pieces required from string-ribbon area = a_9 / a_7

Fig. 28. Flowchart to calculate the proportional area and pieces to be cored from laminate for Hybrid approach

Two sets of samples were sent to two TCLP labs to test for repeatability within a lab and reproducibility between the labs. To avoid damage to the cored samples while shipping to

the testing labs, the samples were kept in small containers and is sealed in a compact cushion shipping box.

3.6 Pros and Cons of Different Sample Removal Approaches

The sample removal approaches have their pros and cons with respect to the sample removal time consumed, variation in the size of the particles removed, variation in the particle size reduced by the labs and proportional samples removed from the distinct areas of the laminate. All these factors have a significant role to play in the variability of the TCLP results. The pros and cons of the different sample removal approaches are presented in Table 6.

Table 6: Pros and Cons of different sample removal methods

Pros/Cons	Coring	Cell-cut	Strip-cut	Hybrid
Pros	- Represents all laminate areas and the maximum particle size is fixed to 9.5mm - Most accurate (but variability issue still significant)	- Least time consuming	- Least time consuming	- Moderate time consuming - Considers cell, non-cell, and string-ribbon areas proportionally
Cons	- Most time consuming	- Non-cell and string-ribbon areas not represented	- Non-cell and string-ribbon areas not represented	- Particle size from the cell area significantly

		- Piece cut by the TCLP lab from the supplied full cell may have different location and orientation - Minimum particle size may vary from one TCLP lab to the other	- Minimum particle size may vary from one TCLP lab to the other	varies and that includes the powdered kerf particles.

3.7 Image Processing of Glass Particles on PV Modules using MATLAB

The purpose of determining the particle size distribution of glass particles on the surface of modules is:

- To demonstrate why samples tested for toxicity should not be of a size greater than 9.5 mm and not crushed to a size less than 1 mm or to micron level in the TCLP labs.

    - According to EPA 1311, "Particle size reduction is required, unless the solid is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm standard sieve" [2].

- To demonstrate the effect of non-uniform glass tempering in a module which leads to non-uniform glass pieces' sizes in different ends of the same PV module.

Image processing was done for five images taken from the glass side of the modules:

- 1st image: Module B

- 2nd image: Module C

- 3rd image: Module D (First image - near the junction box side)

- 4th image: Module D (Second image - opposite corner of the junction box side)

- 5th image: Module E

Two images were taken from Module E to demonstrate the effect of non-uniform glass tempering on the variation of size of glass particles (which lead to huge variation in the TCLP results of coring approach).
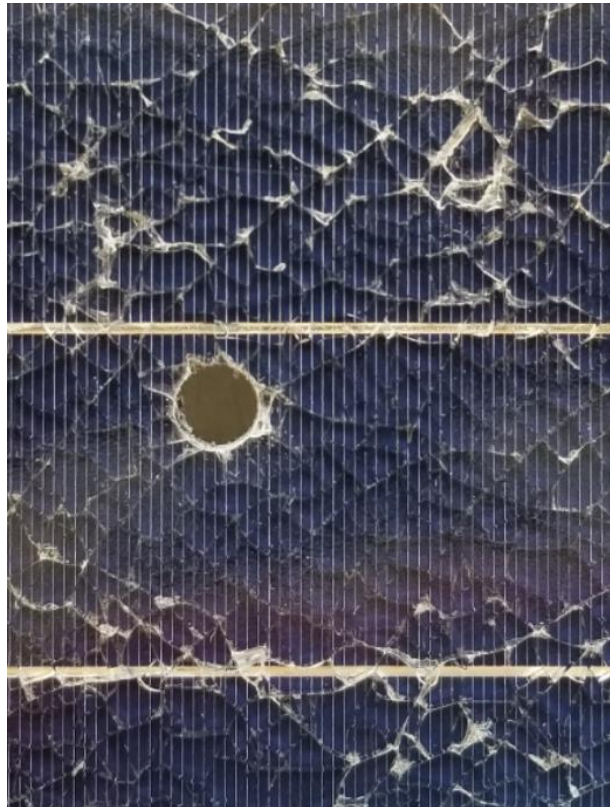
Fig. 29. Image from a PV module for particle size determination

3.7.1 Manual Tracing of Cracks

The images taken from the surface of PV modules have cracks as shown in Fig. 29 which cannot be easily determined and processed using MATLAB. To make image processing easier, to define boundaries, and to color threshold the image, cracks were manually traced in red color (R – 237, G – 28, B – 36) using MS Paint as shown in Fig. 30.
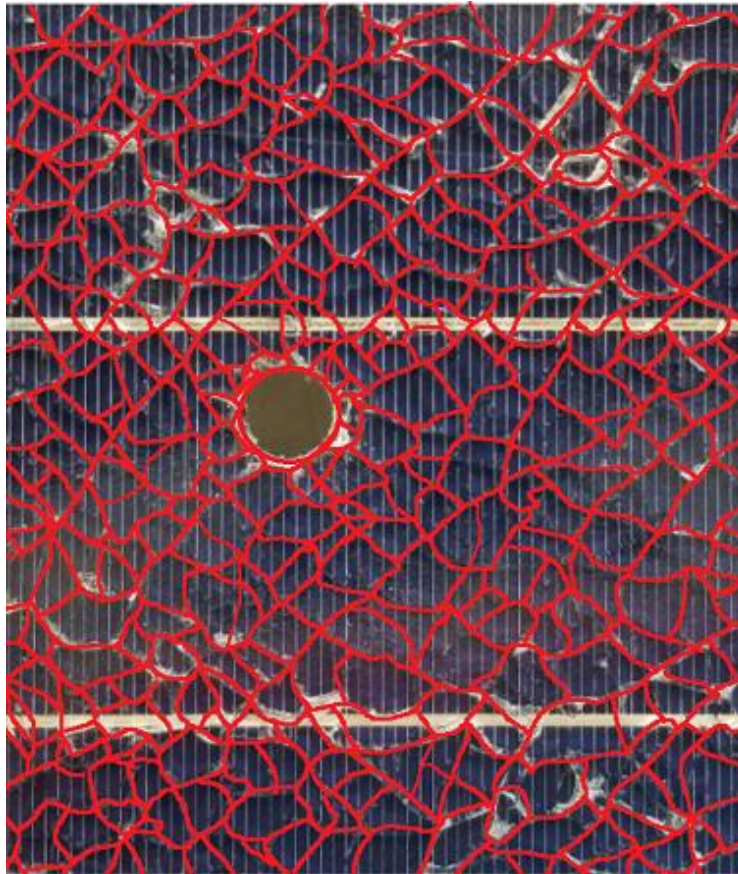
Fig. 30. Manual Tracing of cracks using MS Paint

3.7.2 Particle Size Determination using MATLAB

The image of the manually traced cracks is used for image processing. The traced image is converted to a grey image by eliminating the hue and saturation information while retaining the luminance using the function "rgb2grey". This grey scale is then converted into a binary image using the MATLAB function "im2bw". This image is used to determine the number of cracks and area of each crack.

(a)   *(b)*

Fig. 31. (a) Greyscale image, (b) Binary image of the traced cracks

The MATLAB function "bwconncomp" is used to determine the number of glass particles and the area of the glass particles. For the purpose of normalizing the obtained valu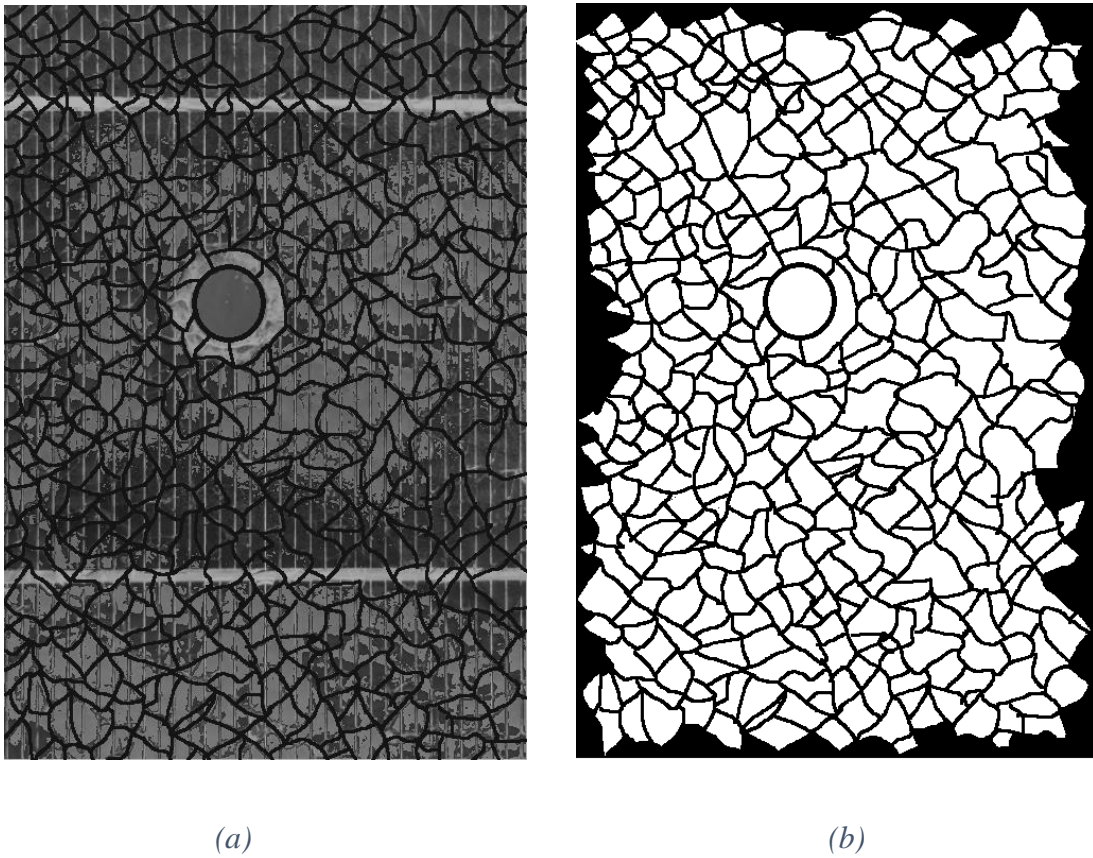es to real values of area, another image of the same pixel size is taken and only the cored area in the image was manually traced as shown in Fig. 32(a). This image is processed using MATLAB and the corresponding binary image is shown in Fig. 32(b).

The diameter of the cored sample is known to be 9.5 mm and the area of the cored area is 70.88 mm^2. The obtained area value in MATLAB and the known cored area can be used as a correction factor to find the original area of the cracks in mm^2. The cored area value in the image of the manually traced cracks obtained through MATLAB is neglected, as it is not a glass piece but the cored area.
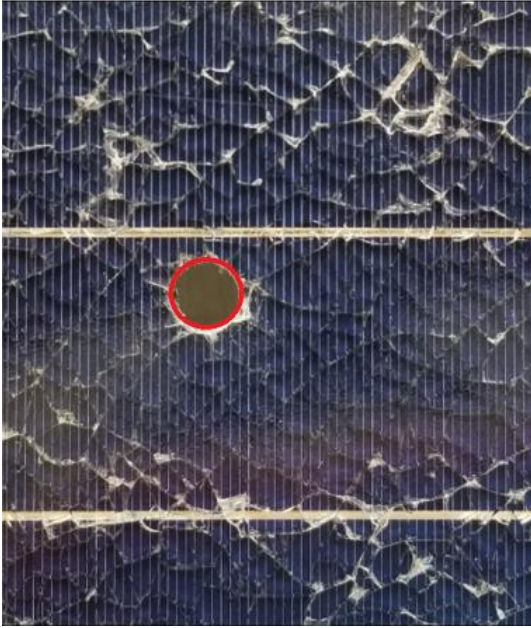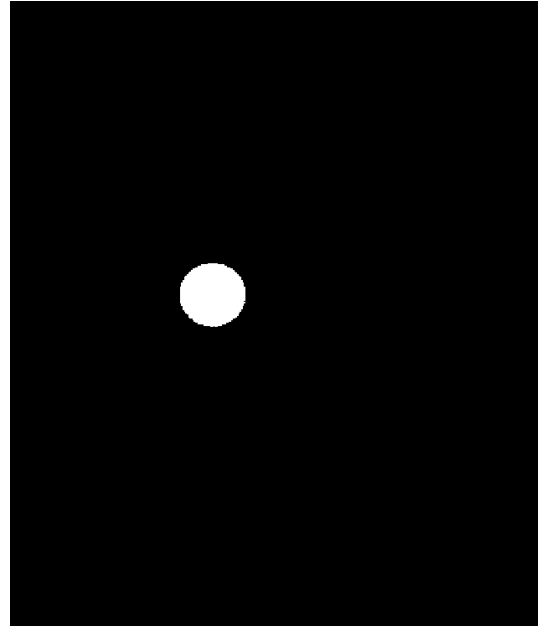
(a)   *(b)*

Fig. 32. (a) Manual traced cored area of the image, (b) Binary image of the processed image

3.8 Image Processing of Different Cored Samples using MATLAB

When there are more cracks and less glass coverage on the surface of the cored sample, more leaching takes place (as the surface area contact is more), and subsequently shows higher result or amount. For example, when 20 pieces are cored from the laminate of the same module, not all pieces have the same amount of glass coverage and the cracks also vary. This also varies from module to module, and from the coring side (glass side or backsheet side). The main purpose of image processing on the cored pieces is to determine the area of glass coverage (which is indirectly proportional to the amount of toxic elements leached).

To determine the variation of glass coverage and perimeter of the cracks, three cored samples were taken as shown in Fig. 33:

> First cored sample – Piece cored from the backsheet side (glass coverage >100%)

> Second cored sample – Piece cored from the glass side (glass coverage <<100%)

> Third cored sample – Piece cored from the glass side (glass coverage < 100%)

(a)   *(b)*   *(c)*
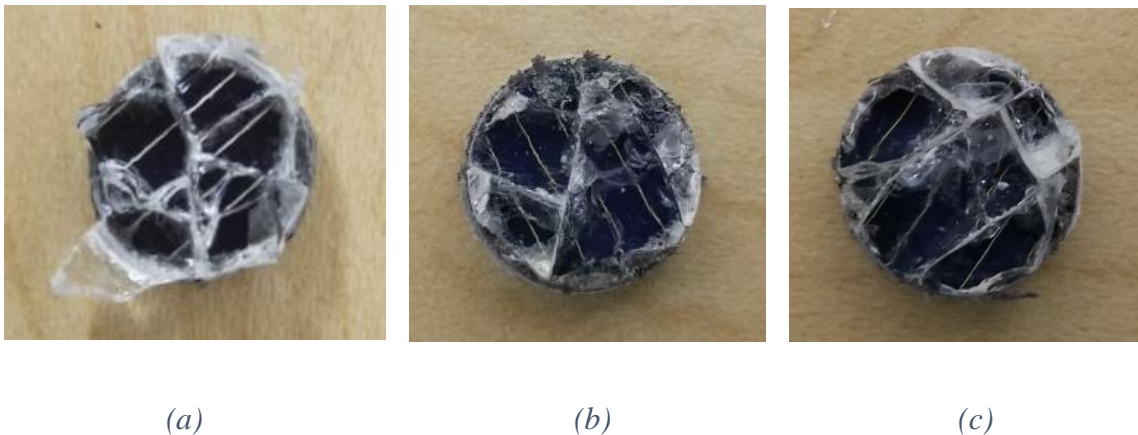
Fig. 33. Different Cored Pieces for Image processing

Image processing of the different cored samples was done using MATLAB. The same procedure is followed as discussed in Section 3.7.1 for manual tracing of cracks. The traced image as shown in Fig. 34(a) is processed using MATLAB to find the number of glass particles and the area of glass particles. The same procedure as discussed in Section 3.7.2 is followed to convert the RGB image to binary image, and to find the correction factor to obtain the area of the glass particles.

(a)   *(b)*
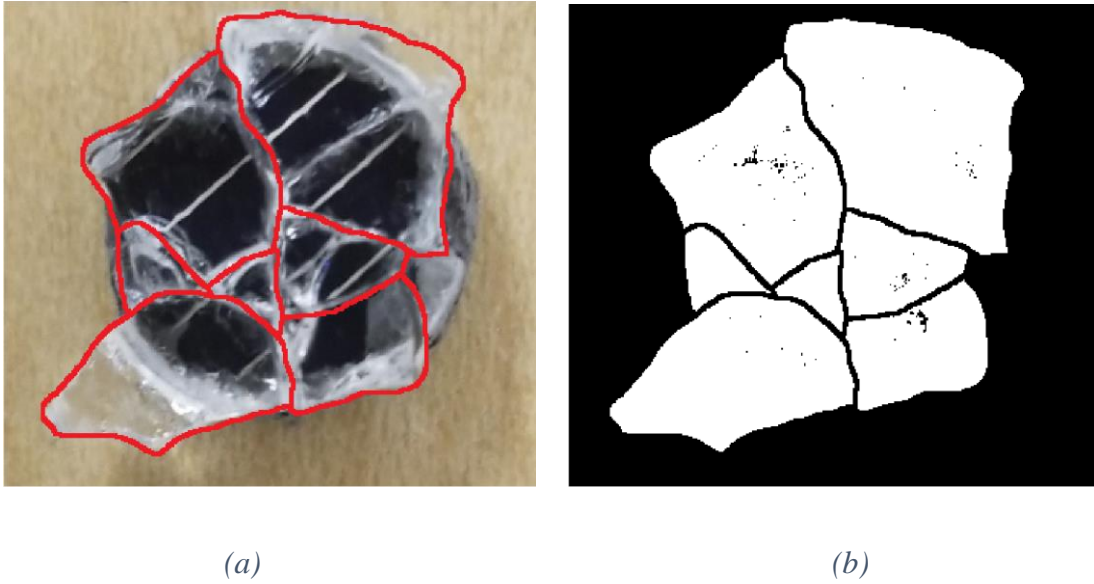
Fig. 34. (a) Manual Tracing of cracks on a cored sample, (b) Binary image of the cored sample

4. RESULTS AND DISCUSSION

4.1 TCLP Results

Samples from the laminate area were removed using the four removal methods: Coring approach, cell-cut approach, strip-cut approach, and hybrid approach. The removal process and TCLP testing of the PV laminate were done in two phases. These samples were sent to two TCLP laboratories to check for the reproducibility between the labs and the same was performed twice to check for the repeatability within the labs.

4.1.1 Phase 1 Testing

Fig. 35. Flowchart showing the total samples removed from 1 manufacturer for phase one

In the first phase, one poly-Si module (module A) was selected. In this module, one set of coring approach, two sets of cell-cut approach and two sets of strip-cut approach were performed as shown in Fig. 35.

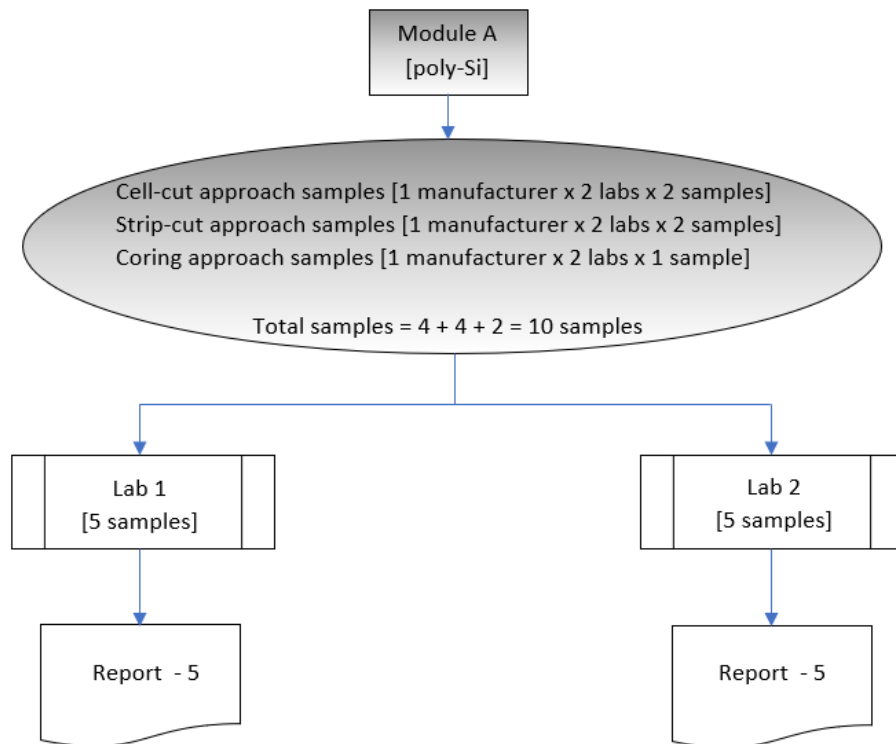The results from the labs for phase 1 are shown in Fig. 36. The variation between lab 1 and lab 2 for the coring approach is minimum as compared to the other approaches but it is still significant. For the first sample set of cell-cut approach (cell-cut approach – 1) sent to the TCLP testing laboratories (the samples weighed between 267g and 277g), no instruction was given to the labs on how to reduce the sample weight, and for second sample set of cell-cut approach (cell-cut approach – 2), clear instructions were given to the labs on how to reduce the sample weight (to cut the sample in a rectangular strip and perpendicular to the cell stringing ribbons). The TCLP laboratories need to cut the samples as they require only 100g – 110g of sample for toxicity testing. As seen the result from Fig. 36 for the cell-cut approach – 1 and 2, there is a huge variation in the result between the labs. This can be due to the inadvertent but biased removal of samples while cutting in the TCLP laboratories.
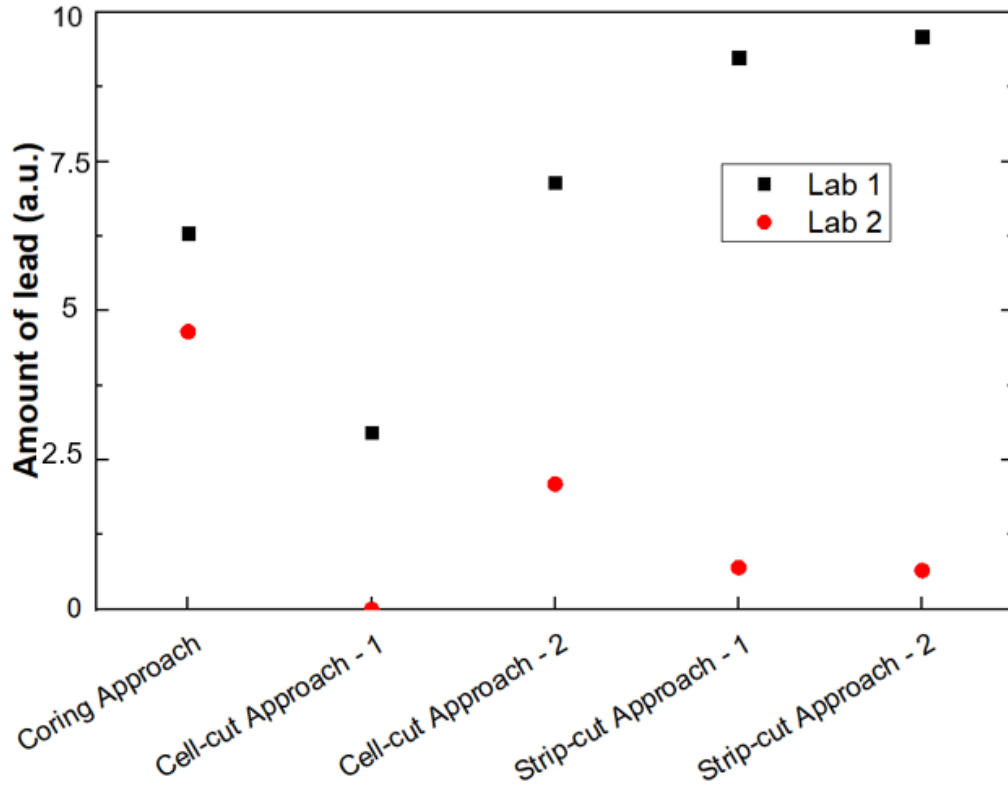
Fig. 36. Comparison of TCLP Results of lead for various sampling approaches of module manufacturer A

As shown in Fig. 37, if the samples are removed along the cell stringing ribbons, more toxicity level will be shown in the result. In contrast, if only the bare silicon solar cells are included in the cut sample excluding the cell stringing ribbons, the toxicity level will be practically zero as the toxic metal (lead) can be found in the string ribbons.
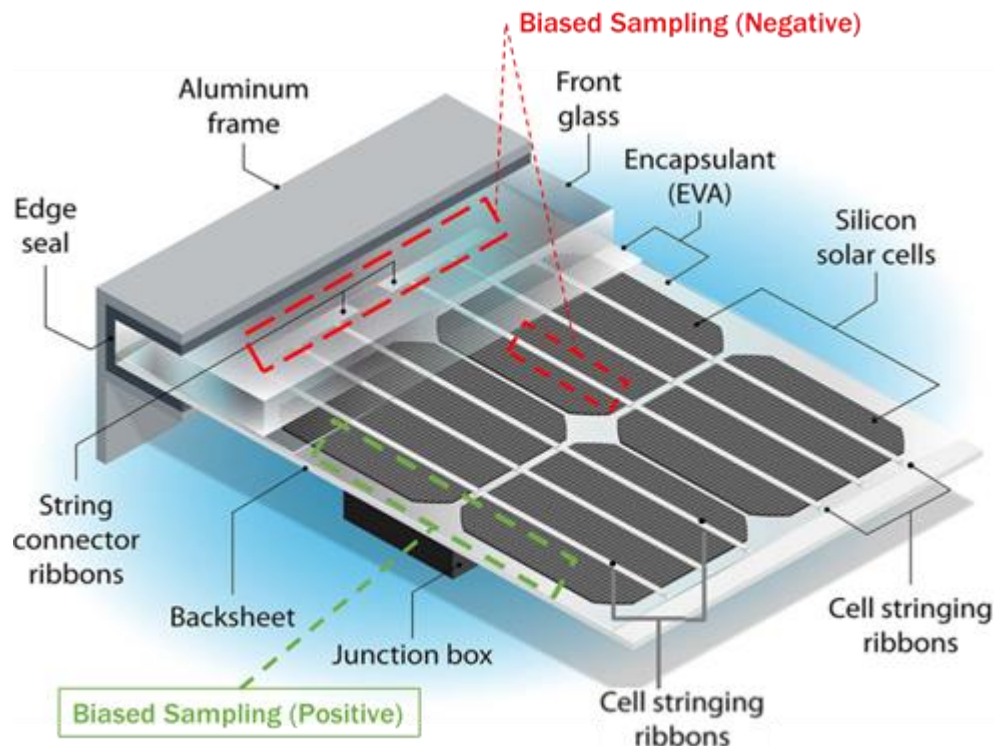
Fig. 37. Module showing the positive and negative sampling (Diagram credit: DOE/EERE)

As seen from the Table 4 (discussed in section 3.1), the solvent, water : sodium hydroxide : acetic acid, liquid : solid for agitation, agitation time, agitation rpm, test temperature are almost similar for both the TCLP testing labs and are in accordance with the EPA Method 1311 standard. The one noticeable point is the sample size. The EPA Method 1311 specifies the maximum size to be 9.5 mm but not the minimum size. The labs do not have a standard procedure on how to reduce the sample, especially when the cell or the strip samples are sent. They may crush the samples to micron level or may reduce the sample such that the sample size is exactly 9.5 mm. These are two extremes in the sample sizes, which may cause huge variation in the TCLP result of lead. When the TCLP labs reduce

the sample to the size of 9.5mm, the surface area contact with the cell-interconnects and

string-ribbon interconnects will be less, and hence less amount of lead is leached into the

extraction fluid. In contrast, when the TCLP labs reduce the sample size to micron level,

the surface area contact with the interconnects will be more, and hence more amount of
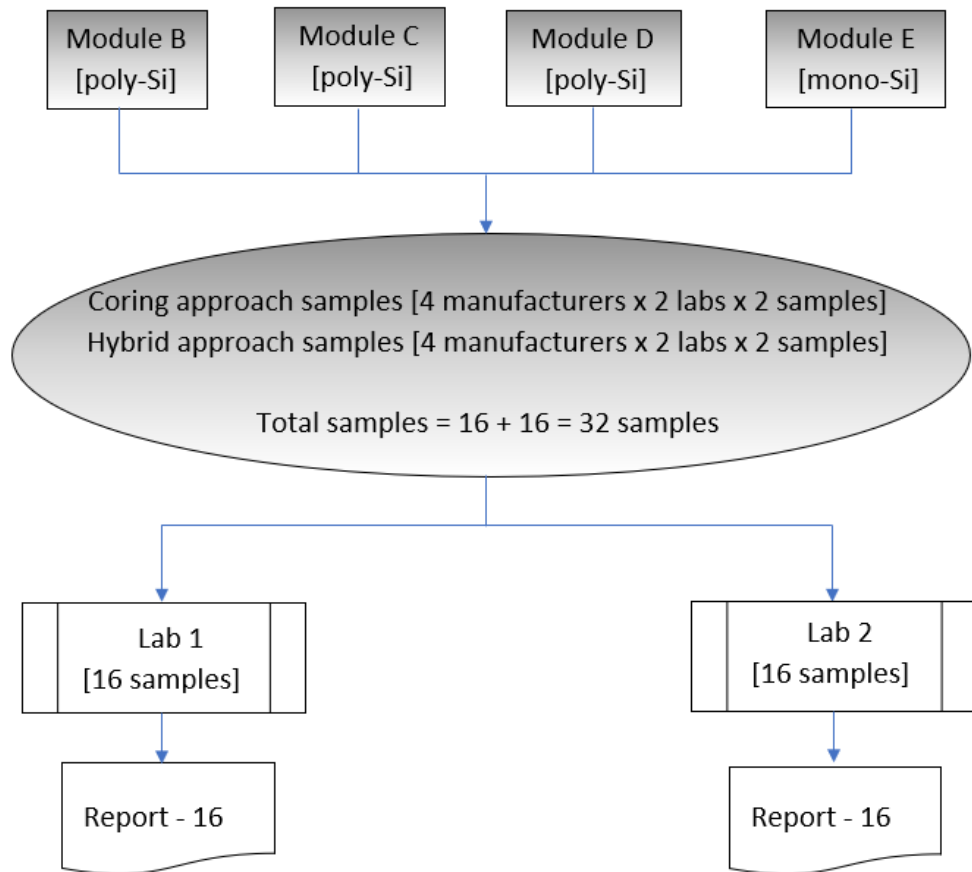
lead will be leached.

4.1.2 Phase 2 Testing

Fig. 38. Flowchart showing the total samples removed from four different manufacturers for phase 2

For the second phase, the toxicity testing of PV modules in the laminate is extended for four different manufacturers (three poly-Si and one mono-Si modules). In all these four module manufacturers, coring and hybrid approaches were utilized and the samples were sent twice (1-2 weeks apart) to the two TCLP testing laboratories to verify the test repeatability within the labs and reproducibility between the labs as shown in Fig. 38.

The test results from the TCLP labs are shown in Fig. 39. The manufacturer E module shows the minimal (practically zero) amount of lead in the laminate for both the coring and hybrid approaches. For the coring approaches of module manufacturers B and C, the variation of TCLP result of lead is <20%. But in case of the module manufacturer D for the coring approach, there seems to be >50% variation in the result of lead even for the coring approach. Although almost all the cored samples have glass coverage of 90-95%, the crack lengths/numbers significantly vary from one cored piece to the other for this manufacturer. This may be due to the non-uniform tempering of the glass of the module (glass particles size variation is discussed in section 4.2). If the cracks are more on the cored sample, more leaching would be expected which in turn would increase the lead content in the leachate. In contrast, if the cracks are less, there would be less leaching expected in the extraction fluid. Thus, even for the coring approach, the test results of the samples could significantly vary from one location to the other of the module depending on the number/length of cracks observed in each of the cored glass pieces.
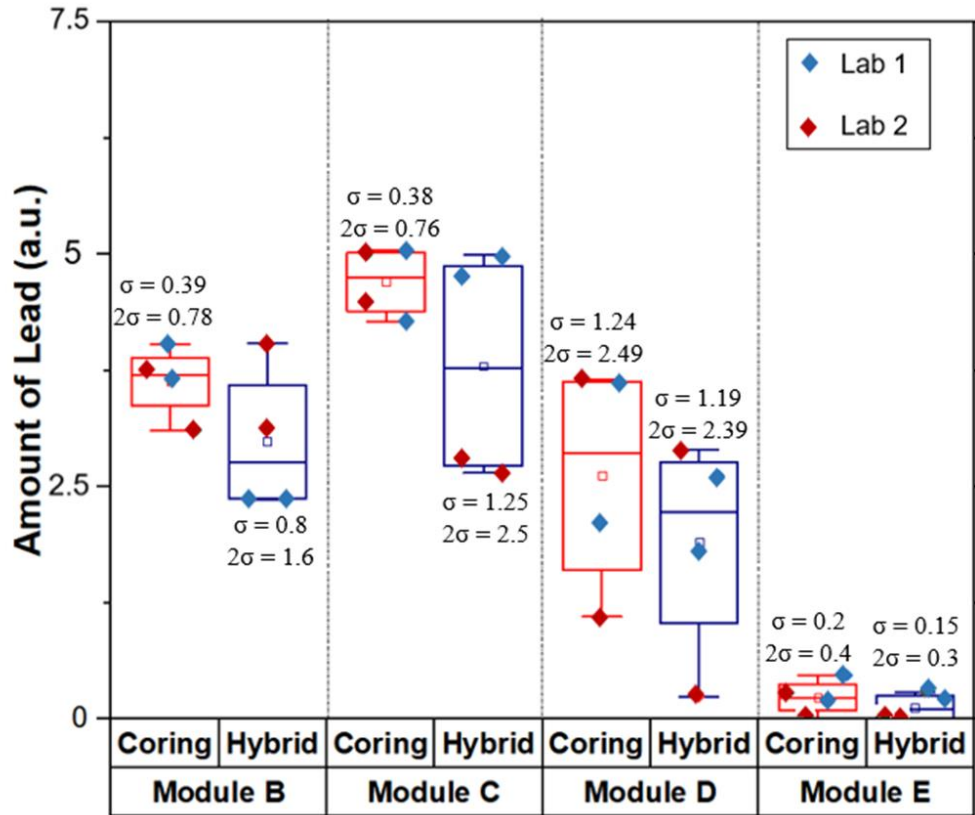
Fig. 39. Lead amount in four different module manufacturers for coring and hybrid approaches (four samples per approach per module)

From the test results of lead for the hybrid approaches of module manufacturers B, C and D, there seems to be >50% variation in the lead content result in the laminate. In the hybrid approach, since the samples are cored very close to each other within the small pre-defined area, the cored glass pieces tend to shatter further into fine pieces leading to a huge variation in the test results. The glass coverage in almost all the cored pieces from the defined strip area was less than 90%. Also, while agitation during the leaching process, more glass pieces are expected to be breaking off from each of the supplied cored pieces leading to much less than 90% glass coverage area. All these issues lead to a huge variation

in the test results and hence the hybrid approach is eliminated from the future considerations.

In the case of coring approach, the variation of toxicity test result is less as the glass coverage on the cored sample is almost same (around 95%). Thus, coring approach seems to be the most unbiased approach, mostly repeatable approach within a lab (except for module D) and reasonably reproducible approach between the labs when compared to the other sample removal approaches presented in this paper. Since the crack length/number significantly vary from one piece to the other, even the coring approach needs to be improved further to reduce the variation/uncertainty in the test results.

The factors for variation of the TCLP results are summarized as below:

- During sample removal
  - Glass coverage area and crack length
  - Sample removal locations
- Before agitation process in TCLP laboratories
  - Sample reduction size (9.5 mm or micron level)
  - Biasing or unbiasing of samples while sample reduction (in case of cell-cut approach)
- Agitation process
  - pH of the extraction fluid (more acidic the solution is, more leaching takes place)
  - Agitation duration and rpm

4.2 Particle Size Distribution of glass particles:

The main purpose of TCLP testing is to accelerate (agitation process) and simulate the leaching process of disposed PV modules in the ground, and to determine the amount of toxic elements leaching to the ground. In this case, crushing of particles by TCLP labs should be equal to the amount of module crushed which experiences when put in a landfill. According to EPA 1311, "Particle size reduction is required, unless the solid is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm standard sieve)" [2].

Table 7: Median, Mean, Max, and Min values of the area of glass pieces in different modules

Area of glass pieces (mm^2)				
	Median	**Mean**	**Max**	**Min**
Module B	9.66	11.71	36.78	1.56
Module C	9.30	10.33	25.82	1.14
Module D - 1	9.36	10.54	34.52	1.27
Module D - 2	7.87	9.81	35.40	1.99
Module E	9.47	11.03	49.46	2.20

The median area of the glass particles in the four broken module images (Module B, Module C, Module D – 1, Module D – 2, and Module E) obtained through image processing is found to be around 9.5 mm^2, which is the amount of glass breakage experienced in the landfill. Thus, if the samples are crushed to micron level, the leaching will be unacceptably

more aggressive than the field PV module leaching process. For module D, the median area of the glass particles from the two images is found to be 9.3 mm^2 and 7.9 mm^2. This seems to indicate that there is potential non-uniform tempering of the glass in this module, which led to the variability in the TCLP results for the coring approach as seen in Fig. 40. The Fig. 40 shows the variation in the area of the glass particles for various modules.
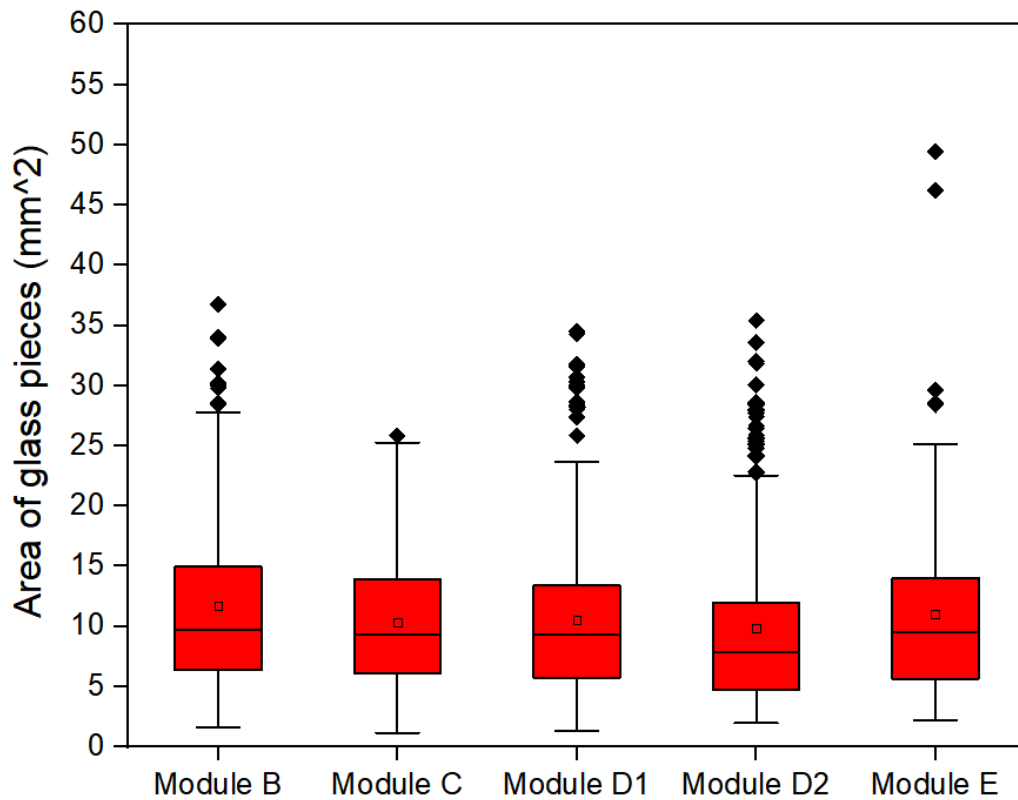

Fig. 40. Variation in the area of glass particles for various images

A perfect cored piece has to have a glass coverage of about 95% - 100%. The Fig. 41 shows the glass coverage area (%) of three cored pieces. The cored piece – 1 is the piece cored from the backsheet side. The cored pieces – 2 and 3 are the pieces cored from glass side.
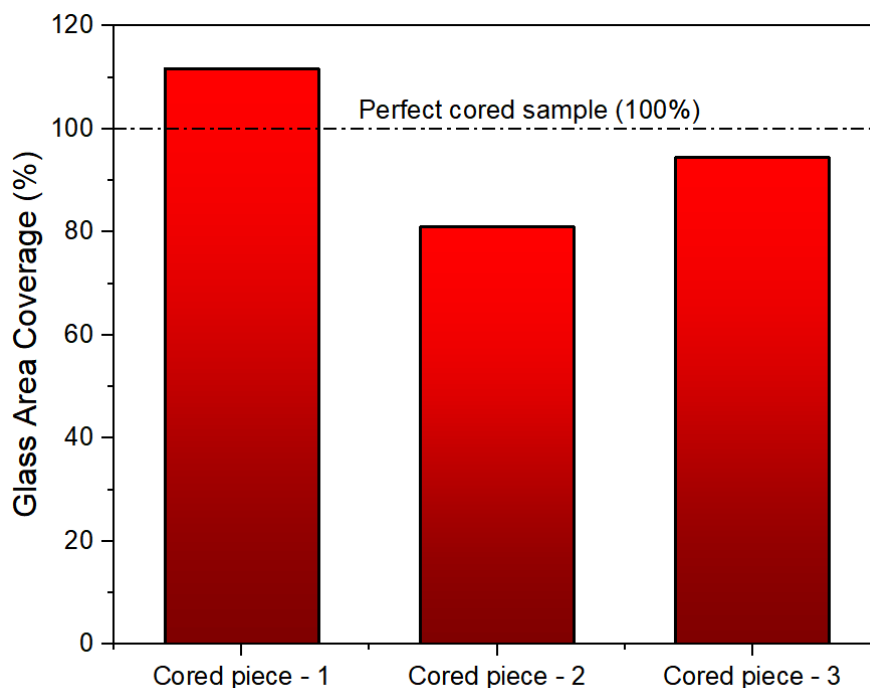
Fig. 41. Glass coverage area for three cored pieces

Coring samples from the backsheet is not recommended, as the cored pieces tend to have a glass coverage area higher than 100%. In case of the cored piece – 2, the glass coverage area is around 75%. In the remaining 25% area, the cell interconnects and the fingers are directly exposed to the extraction fluid, and hence the leaching is expected to be higher. For the cored piece – 3, the glass coverage area is about 95%. This is nearly a perfect cored

piece for TCLP testing. Moreover, the total crack length from one piece to another could also differ for the same glass coverage area. All these factors are expected to influence the accuracy of the end test results (mg/L) even for the best method, the coring method, within the same TCLP laboratory. Therefore, to improve the repeatability and reproducibility of test results, it is recommended to reject all the pieces which have the glass coverage area lower than 90% or 95%.

5. CONCLUSION

The volume of decommissioned PV modules will increase as the global PV market increases. The cumulative global PV waste streams are expected to reach 43,500 – 250,000 metric tons by the end of 2020, and these volumes are bound to increase further. Since the average life of a PV module is typically 25 years, within next 6-7 years, there will be a great demand for PV recycling facilities. Due to the drastic increase in the end-of-life PV modules, these modules may not be left in the landfills. When they are left in the landfill, the toxic elements, if any, from the PV modules could leach into the ground and contaminate the soil and groundwater.

The accurate quantification of toxic elements in a PV module will allow PV module manufacturers, plant owners, and operators, and other industry stakeholders to identify suitable end-of-life disposal options. Development of an acceptable sample removal method and consistency in sample particle sizes are critical needs to accurately and reproducibly quantify levels of toxic elements during TCLP testing. The main objective of this thesis is to develop unbiased sampling method for laminate and reducing the variability in the TCLP results from the laboratories. Four sample removal methods were applied to the laminate for five different module manufacturers and the results were compared reproducibility between the labs and repeatability within the labs.

The following conclusions were drawn from the TCLP results of various sampling methods:

- The cell-cut approach cannot be followed due to the following reasons:

- There is uncertainty on how the testing labs locate the sample for testing from the whole cell (leads to positive biasing, negative biasing or unbiased) as the testing labs require only 100-110g for testing.

- There is uncertainty on how the sample size is reduced (whether to 9.5mm or to micron level). The EPA 1311 method specifies only the maximum size of the sample to be tested, but not the minimum size.

- The strip-cut approach cannot be followed due to the following reason:

  - There is uncertainty on how the sample size is reduced (whether to 9.5mm or to micron level).

- The hybrid-cut approach cannot be followed due to the following reasons:

  - The glass coverage varies from one cored sample to another (less than 90%) during sampling.

  - There is a significant variation in the particle size (cored pieces and kerf particles).

- The coring approach can be followed for the following reasons:

  - The sample size is nearly consistent (9.5 mm).

  - The weight of the samples sent are 100-110g and are in accordance with EPA 1311 method.

The variation in the TCLP results of coring approach is the least when compared to the four explored sampling methods though the variability in the coring approach is not acceptably low. To further reduce the variability of TCLP results of coring approach to an acceptable level, additional improvements are needed. From the image processing of glass

particles from different modules, it was clear than the particle size reduction below 9.5 mm^2 is not reasonable for PV modules.

After coring one sample in the coring approach, the coring bit is removed from the coring machine to remove the cored piece which is stuck inside the bit. This takes a majority of the time while removing samples from laminate by this method. In future, a faster method can be developed to remove cored piece from the coring bit instead of removing the coring bit each time a sample has been cored.

According to EPA 1311 method, a sample has to have a narrowest dimension of 1 cm to pass through a standard sieve. In future, this can be verified by image processing, for the samples cored to check whether the samples are of size 1 cm in their narrowest dimension. Also, the crack lengths can be found out on different cored samples by image processing and can be checked for consistency between different cored samples. If the crack lengths are same and glass coverage area on different cored samples are consistent, the variation of TCLP results can be greatly reduced.

Some of the recommendations to reduce the variability in the TCLP results are:

- After coring from the glass side of the laminate, the cored sample gets stuck inside the coring bit and is hammered to remove the sample. Sometimes the hammering process damages the cored samples and more creates more cracks. To reduce this damage, polyethylene foam (sheet) can be kept inside the coring bit and then the sample can be cored. When trying to remove the cored sample which is stuck inside the coring bit, hammering is done from the polyethylene side of the coring bit and

the glass surface on the cored sample will not be damaged due to the presence of the foam and there will be less cracks on the surface of the cored piece.

- After coring all the pieces (proportionally, representing the whole of laminate area), it can be completely crushed to micrometer level and then sent to the TCLP labs. This micrometer scale overestimates the amount of crushing a module would experience when put in a landfill, and it will not be the exact amount of toxic elements leaching to the ground. But, this will help to verify whether the variation in the toxicity results are due to sampling process or testing in the TCLP laboratories.

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