Standardized Sample Extraction Procedure for TCLP Testing of PV Modules

by

Raghav Krishnamurthy

A Thesis Presented in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Approved July 2017 by the
Graduate Supervisory Committee:

Govindasamy Tamizhmani, Chair
Devarajan Srinivasan
Joseph Kuitche

ARIZONA STATE UNIVERSITY

August 2017

ABSTRACT

Solar photovoltaic (PV) deployment has grown at unprecedented rates since the early 2000s. As the global PV market increases, so will the volume of decommissioned PV panels. Growing PV panel waste presents a new environmental challenge, but also unprecedented opportunities to create value and pursue new economic avenues. Currently in United Stated there are no regulations for governing the recycling of solar panels and the recycling process varies by the manufacturer. To bring in PV specific recycling regulations, whether the PV panels are toxic to the landfills, is to be determined. Per existing EPA regulations, PV panels are categorized as general waste and are subjected to a toxicity characterization leaching procedure (TCLP) to determine if it contains any toxic metals that can possibly leach into the landfill. In this thesis, a standardized procedure is developed for extracting samples from an end of life PV module. A literature review of the existing regulations in Europe and other countries is done. The sample extraction procedure is tested on a crystalline Si module to validate the method. The extracted samples are sent to an independent TCLP testing lab and the results are obtained. Image processing technique developed at ASU PRL is used to detect the particle size in a broken module and the size of samples sent is confirmed to follow the regulation.

To,
My parents, K.V. Krishnamurthy, and Dr. Chitra Krishnamurthy, and other friends and family members for their constant support and love.

ACKNOWLEDGMENTS

I would like to first give my thanks and appreciation to Dr. Govindasamy Tamizhmani for accepting me into his lab and providing me all the amazing opportunities I've had and for his constant support throughout my thesis work. The work I have done in his lab has allowed for me to get hands-on-experience in almost all aspects of the PV systems and I consider myself very fortunate to have been able to learn under him, as well as from both current and past students in the lab. I thank my committee members, Dr. Kuitche and Dr. Srini, for their help and support along the way. I would like to thank my fellow lab students for their support, and I would specifically like to thank Raginee Yadav for her help in developing the image processing algorithm. I would also like to thank Sai Tatapudi, our technical lab manager, for his support and guidance. Last but not the least, I would like to thank all the other students that I have had the pleasure of working with at ASU-PRL.

TABLE OF CONTENTS

Page

CHAPTER Page

CHAPTER Page

LIST OF FIGURES

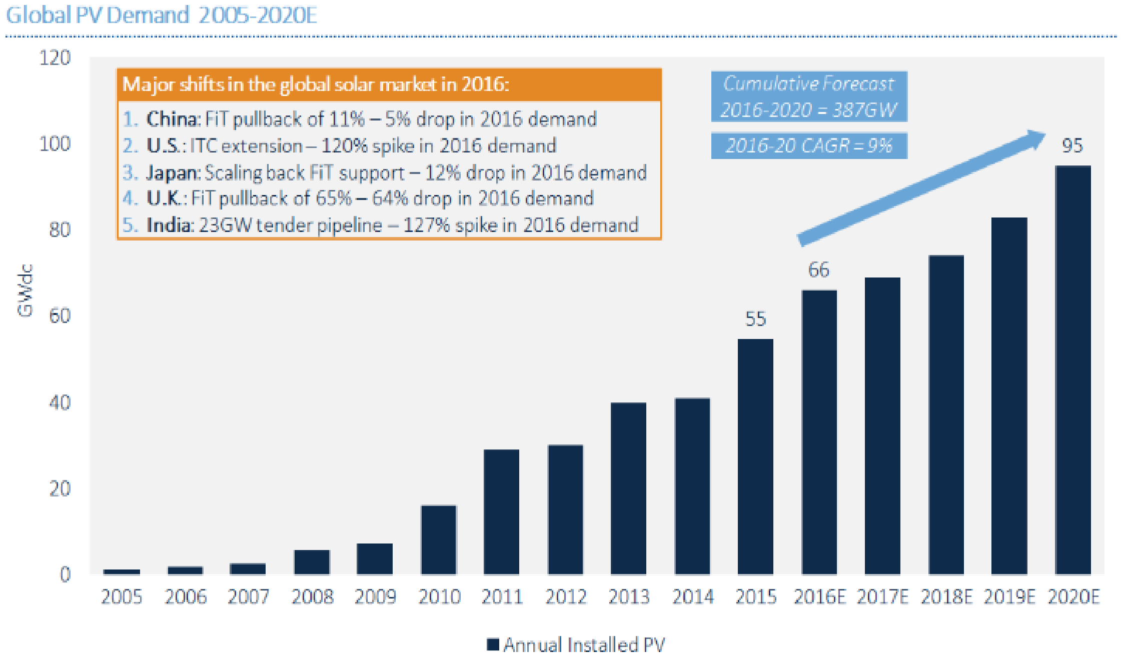
LIST OF TABLES

1. INTRODUCTION

1.1 Background

Solar energy is the primary stakeholder in the renewable energy field. Generating energy through photovoltaic (PV) technology is one of the primary methods of emission free power generation. The PV industry is expanding rapidly and this has increased the demand for raw materials worldwide. To understand the environmental impact of a product, companies need to study the full cycle of the product, from cradle to-grave. Coincidentally, in the recent years, the first PV systems have reached the end of their days and it is estimated that by the end of 2016, a considerable number of PV modules will have fallen into disuse and the resulting amount of PV waste is expected to increase exponentially. The electronics industry failed to account for their product's end-of-life in the manufacturing process and created widespread toxic chemical pollution. The solar energy industry can avoid a similar mistake by not only accounting for the materials used during manufacturing, but also the transportation, disposal, recycling and reuse of these panels. By means of recycling, valuable raw materials can be recovered, thus reducing the demand for primary raw materials.

The viability of a recycling program for any product depends on the level of waste stream. As shown in Figure 1 below, the solar photovoltaic (PV) market grows at a very high rate around the globe. In 2016, the three largest market shares are projected to be from United States (24%), China (17%) and Japan (15%). The fast growth of the industry shown in this figure clearly indicates that the PV recycling could soon become a major issue in Europe, US, China and Japan.[1]



Source: Global Solar Demand Monitor, Q2 2016

Figure 1 Global solar PV market growth between 2005 and 2020 (estimated).

1.2 Problem Statement

With typical PV module lifespans of 20 years, some older utility-scale PV power plants in the US are soon facing the challenge on how to dispose of large quantities of PV modules in an environmentally friendly way. Some PV modules may contain hazardous materials, such as lead, PBDE (Polybrominated diphenyl ether), chromium, and cadmium. It is estimated that more than 80% of materials from PV modules can be recycled. Unlike Europe, in the US, there are no federal, state, or local regulations requiring PV module recycling. Due to the current low volume of PV modules reaching end-of-life, PV recycling research has been slow in recent years. However, with a rise in large utility-scale PV power plants being deployed in the US and examples of economically and technologically feasible recycling models that have been implemented overseas, interest in PV recycling research has been increasing.

There is disagreement on the environmental costs of dumping PV modules in the landfill. Independent evaluation of the toxicity of PV modules in the landfill environment is needed to understand the different PV technologies. A PV recycling program in the US will likely require regulation, which levels the playing field for all stakeholders in the PV industry. A regulated recycling program will likely entail a robust collection system that gathers PV modules from sites of waste generation and transports it to a cost-effective recycling plant.

1.3 Objective

This study will evaluate the need and feasibility of developing a robust PV recycling program in the US by determining the hazard status of selected PV panels and by examining the current state-of-the-art in PV recycling regulation, collection systems, and technology. In addition, this study will collect all the technical information to develop a PV-specific toxicity test procedure and a standardized sample extraction process.

The major objectives of the project are:

1. to provide information that will aid in the development of regulations to promote environmentally friendly PV recycling
2. to collect the technical information needed to develop a PV module-specific sample extraction procedure for TCLP (Toxicity Characteristic Leaching Procedure) testing

3. to perform TCLP tests on the recent commercial modules retrieved from the field and/or collected from other sources

2. LITERATURE REVIEW

2.1 PV Recycling

With increasing populations and increasing photovoltaic installations, there is an associated increase in accumulated material waste from the solar modules and other balance of system components. It is more economically favorable to discard and replace defective modules with newer ones than to recycle them, because of the low cost of solar modules. Thus, there is increasing environmental pollution (terrestrial toxicity, marine toxicity, human toxicity, metal depletion, particulate matter formation etc.) Large-scale PV deployment in the US has only occurred in the past ten years. Thus, cumulative end of life PV waste volumes in the US are expected to remain low at the end of 2016 at 6,500-24,000 t. In 2030 cumulative waste is projected to rise to between 170,000 t and 1 million t and then possibly increase sevenfold to 7.5-10 million t in 2050.[1]

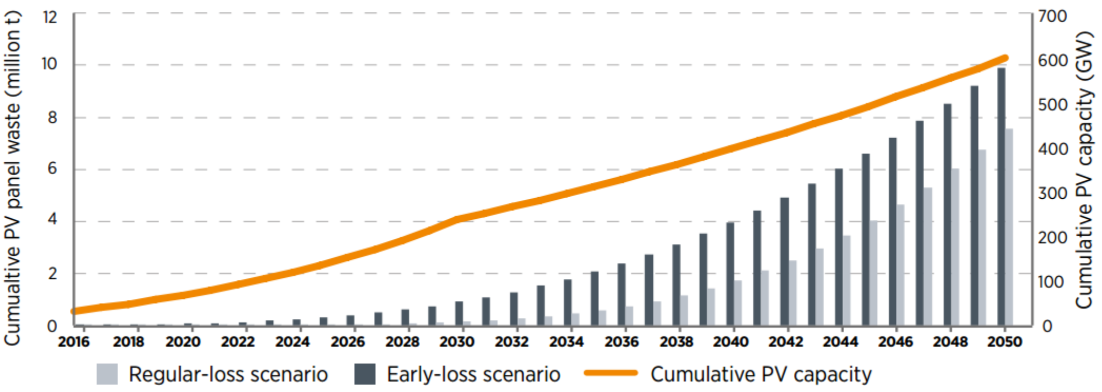


Figure 2 End-of-life PV panel waste volumes for the US to 2050[1]

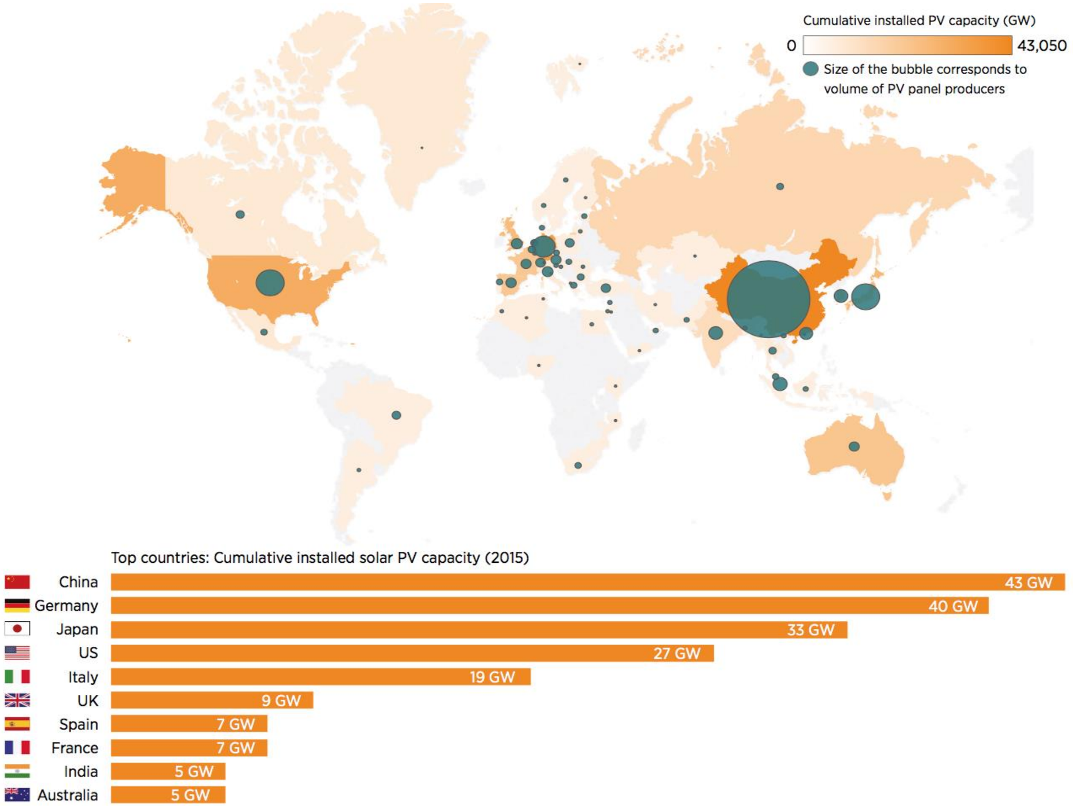


Figure 3 Cumulative PV capacity installed globally[1]

Many non-PV industry members contend that PV modules should be recycled at their end of life. Materials that can be recovered from PV modules primarily include the aluminum frame, module glass, and copper from the leads and junction boxes. For Si and non-Si alike, PV module recycling typically involves removing the frame and connectors, shredding the module, and separating the glass from the silicon and back sheet. PV module manufacturing techniques are unique in a way that makes module recycling technologies slightly different from other industries like electronics waste recycling or flat-glass recycling. The recycling process can be divided into three distinct categories viz, i) regulations ii) technologies iii) collection systems

2.1.1 Recycling regulations

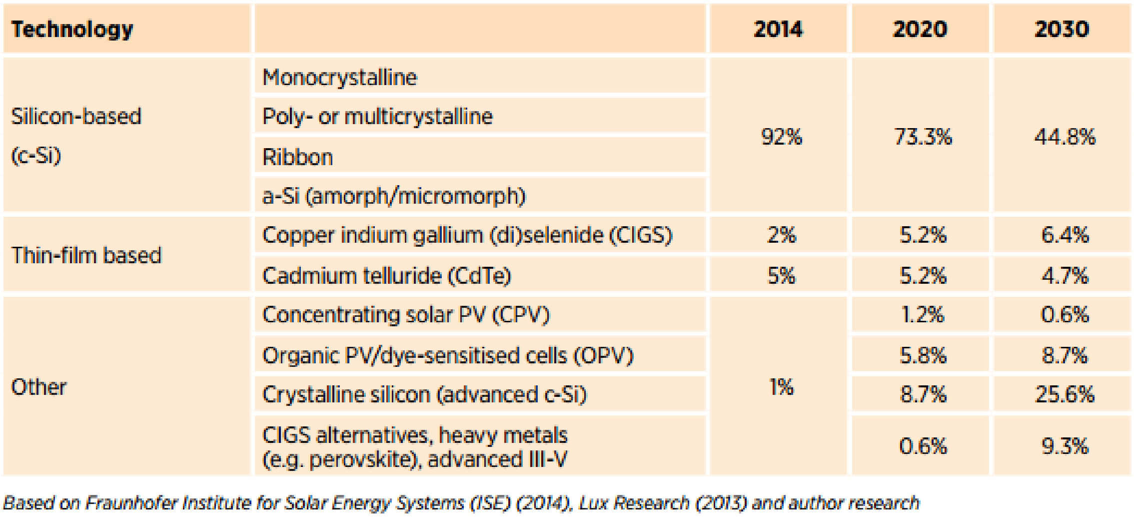
Developing an end of life management scheme for PV not only involves recovery and collection but also the recycling targets and the regulations to support them. The European Union is the only jurisdiction that has developed a set of regulations and policies for the end of life management of PV. Currently in United Stated there are no regulations for governing the recycling of solar panels and the recycling process varies by the manufacturer but, per the Silicon Valley Toxics Coalition (SVTC), they often fall under regulations for waste disposal and hazardous waste. Hence, PV panels must be disposed of in line with the Resource Conservation and Recovery Act (RCRA, 1976) that is the legal framework for managing hazardous and non-hazardous solid waste.[2] The RCRA regulates the disposal of all solid wastes and sets strict guidelines for record keeping, labeling, packaging, transportation, siting, inspections, training, and emergency planning for the generation, transport, storage and disposal of hazardous wastes. To be deemed hazardous by regulators, decommissioned or defective solar panels must fail to meet the US Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedures (TCLP) standards in accordance with the RCRA, or on applicable state policies like the California’s Hazardous Waste Control Law (HWCL). Despite California's HWCL being stricter than federal regulation for hazardous waste, California which has the largest PV installations in the US, does not classify solar modules as hazardous waste.[3] This entails that modules can be directed to landfill after end of useful life.

From a regulatory point of view, PV panel waste still largely falls under the general waste classification. PV panel waste classification follows the basic principles of waste classification. This also considers material composition by mass or volume and properties of the components and materials used. In 2015 two-thirds of PV panels installed across the world were c-Si panels.[1] Typically, more than 90% of their mass is composed of glass, polymer and aluminum, which can be classified as non-hazardous waste. However, smaller constituents of c-Si panels like tin, lead, copper, zinc etc. could be potentially hazardous to the environment. Hazardous materials need treatment and may fall under a specific waste classification depending on the jurisdiction. Different jurisdictions, such as Germany, the US or Japan provide different threshold values for the allowable leachate concentrations for a waste material to be characterized as nonhazardous waste.[4]

In a study on end-of-life management and recycling of PV modules, some long-term environmental strategies for solar cells are discussed. An idea of recycling the solar panels is proposed based on the current collection/recycling infrastructure and emerging recycling technologies. The study indicates that technologies already exist for the recycling of PV modules and the costs associated with recycling are not excessive. Cadmium is considered carcinogenic and is extremely toxic by EPA and the US Occupational Safety and Health Association (OSHA). The environmental codes adopted by solar industries are managed by recognized standards such as ISO 140001 and the Eco Management and Audit System (EMAS). Most environmental standards are Environmental Permits and Reporting, Pollution prevention and Resource reduction, Hazardous Substances, Wastewater and Solid Waste, Air Emissions and Product Content Restrictions.

2.1.2 Recycling technologies

To achieve optimal waste treatment for the distinct PV product categories, the composition of PV panels needs to be taken into consideration. PV panels can be broken down per the technology categories shown in Figure. The different technology types typically differ in terms of materials used in their manufacturing and can contain varying levels of hazardous substances that must be considered during handling and processing.



Technology		2014	2020	2030
Silicon-based (c-Si)	Monocrystalline	92%	73.3%	44.8%
	Poly- or multicrystalline			
	Ribbon			
	a-Si (amorph/micromorph)			
Thin-film based	Copper indium gallium (di)selenide (CIGS)	2%	5.2%	6.4%
	Cadmium telluride (CdTe)	5%	5.2%	4.7%
Other	Concentrating solar PV (CPV)	1%	1.2%	0.6%
	Organic PV/dye-sensitised cells (OPV)		5.8%	8.7%
	Crystalline silicon (advanced c-Si)		8.7%	25.6%
	CIGS alternatives, heavy metals (e.g. perovskite), advanced III-V		0.6%	9.3%

Based on Fraunhofer Institute for Solar Energy Systems (ISE) (2014), Lux Research (2013) and author research

Figure 4 Market share of PV panels by technology groups

To understand or develop a recycling program, a solar PV industry must account for their product's total life cycle including the materials of different components used to manufacture a PV module. Material properties play an important role in recycling program not only from an environmental aspect but also from an economic stand point of view. As part of the decommissioning process the recycling process of PV modules depending on the type of technology has been studied extensively. The basic materials used to manufacture a PV module based on different technologies are discussed below.[5]

a) CRYSTALLINE SILICON MODULE:

A typical crystalline silicon module consists of four main components: the front cover, encapsulant, solar cells and rear layer called tedlar. These modules also consist of a frame along the outer edge. The front cover is commonly made of glass. Tempered, low iron content glass is preferred as it has required properties such as high transmittance and self-cleaning properties. Soda-lime glass or boro-silicate glass is used. Boro-silicate is a more expensive option. An anti-reflective coating mainly layers of silicon di-oxide (SiO_2) is used on the glass to reduce the reflection. The commonly used encapsulant material is ethyl vinyl acetate (EVA) which acts as an adhesive. In solar cells as this technology name suggests, silicon material is used which may either be a mono-crystalline or polycrystalline technology. The rear layer is a tedlar film which is made from polyvinyl fluoride. There are other materials like silver, lead used in interconnects, bus bars, finger contact and aluminum is used in the frame.

b) CADMIUM TELLURIDE MODULE (CdTe):

CdTe thin film module typically consists of five main layers: First layer is glass where Soda-lime glass or boro-silicate glass is used. The second layer is transparent conducting oxide (TCO) which consists of tin doped indium oxide (ITO). The third layer is an n-type semi-conductor cadmium sulphate and it is followed by a p-type semiconductor cadmium telluride. The last layer is back contact which is made up of different materials. Copper gold and copper graphite combinations are used previously but Sb_2Te_3 and As_2Te_3 layers are commonly used these days. The final step in forming the back contact is a coating of molybdenum. Treating of cadmium layers with chlorine is an integral part of this manufacturing process which is done by evaporating $CdCl_2$.

c) COPPER INDIUM GALLIUM SELENIDE MODULE (CIGS):

Commonly known as CIGS module, it is a thin film technology. The basic structure of this module starts with a common substrate the soda lime glass. The next layer is a transparent front contact which is a mixture of ZnO and Al which acts as a semiconductor. Al is used to increase the n-type doping. A heterojunction is formed between ZnO and CIGS semiconductors which are separated by layers of intrinsic ZnO and a layer of CdS. The next layer would be a coating of molybdenum which acts as a back cover and followed by the glass substrate.

d) AMORPHOUS SILICON MODULE:

Amorphous silicon (A-Si) module is also a thin film module. Construction of this thin film is like that of the other thin films with only a change in semi-conductor material. A soda lime glass is at the top followed by transparent conducting oxide made of tin doped indium oxide (ITO). A heterojunction is formed between p-type A-Si (hydrogenated) and n-type C-Si which are separated by a layer of intrinsic A-Si. Then similar layers of intrinsic A-Si and n or p-type A-Si are added followed by a layer of transparent conducting oxide.

2.1.3 Recycling collection systems

The main hindrance to PV recycling is the lack of a recycling infrastructure. This infrastructure should have two main parts: a method of pick-up and transportation of spent modules, and large-scale recycling centers to receive them. Due to the current widespread and decentralized network of solar energy production, collection of the end-of-life modules is the more difficult component of establishing a comprehensive PV recycling system. However, three solutions have been proposed to address this problem.

1) Collection and recycling of PV modules could be undertaken by utility companies, PV manufacturers, or electronic recycling centers. Utilities that own large solar arrays for power generation would be responsible for recycling their own PV modules or transporting them to a recycling center. Unfortunately, the number of utility companies owning large solar arrays is low, therefore this method would only provide for recycling of a small fraction of the total PV modules in use. Eg: First Solar
2) Manufacturers of PV modules would undertake the task of dismantling and transporting the end-of-life modules to a recycling center that supports other electronic waste as well. The manufacturer or consumer could pay the transportation costs, and the recycling center would profit from the sale of the recovered metals and silicon. This is like the existing method used by the electronics industry.
3) The most feasible method for private owners, though, is one like that used by the battery industry. In this, a collection group utilizes reverse retail chains or periodic pick-up to receive used PV modules. Consumers either bring their used PV modules to designated drop-off sites, or call for a truck to arrive on location. The modules would then be delivered to large recycling centers.

2.2 PV Recycling in Europe

Europe has recognized the need to recycle and dispose responsibly PV modules from end of life systems. Under the WEEE Directive (Waste Electrical and Electronic Equipment) of 2014, Europe has made collection and waste treatment of solar modules into a legal obligation.[6] The WEEE directive, before it was revised only covered electronic waste and batteries but since it has recognized the need for responsible recycling of solar PV modules, it has classified PV modules as electronic waste or e-waste. A joint program started in 2002 in Europe by the German Federal Ministry for the Environment to make module recycling more environmental friendly and efficient. It was responsible for the implementation of the Electrical and Electronic Equipment Act (ElektroG) for PV modules. The highlights of the ElektroG are given below

Motivation:

1) Recycle and reuse raw materials
2) Prevent hazardous materials like Cd, Hg, Pb from entering the environment

Implications:

1) Producers are obligated to take their PV modules out of the market
2) The take-back service must be free of charge for the private users of the PV modules
3) Recycling and reusing must be included in the manufacturer’s cost calculation
4) Prohibition of exporting materials from end of life modules out of the country

Working:

1) Private members/users deposit PV modules at municipal take back points

2) Manufacturer takes module to a certified recycling facility where they are recycled free of cost
3) Recycled products are sold back to the manufacturers at subsidized prices
4) Non-reclaimable products are incinerated/disposed of accordingly

2.3 Existing PV recycling technologies

2.3.1 First Solar

First Solar is an American company that was formed in 1999, and launched production of CdTe based PV commercial products in 2002. Currently, First Solar makes up most the CdTe based PV market and for this project First Solar can be used as a model company in this industry. Furthermore, it is the only U.S. based PV company that has implemented a recycling program without it being a mandatory requirement. This collection and recycling program involves three steps: registering each module that the company sells, collecting these modules once they are decommissioned and recycling the modules to recover materials. [7] The company also pays all packaging and transportation costs associated with the collection of the decommissioned modules. This program is a useful model as it covers the most environmentally dangerous photovoltaic-related solid waste and provides an example for other CdTe manufacturers. However, this program is only designed to recycle solar cells that First Solar has manufactured, so policy would need to ensure that each company also instituted such a program. The company has recycled around 48,000 metric tons to date, and does recycling in all its manufacturing plants, scalable to accommodate future high volumes. Roughly 95 percent of the semiconductor material in its modules is recovered along with 90 percent of the glass. Following gives a brief idea of the step by step procedure followed at First Solar.

1) Modules are sent to a hammer mill where it is crushed and hammered to small pieces.
2) The semiconductor material is separated from glass and other materials by acid treatment and is used to form new wafers
3) The remaining material is used to form the glass for the new module

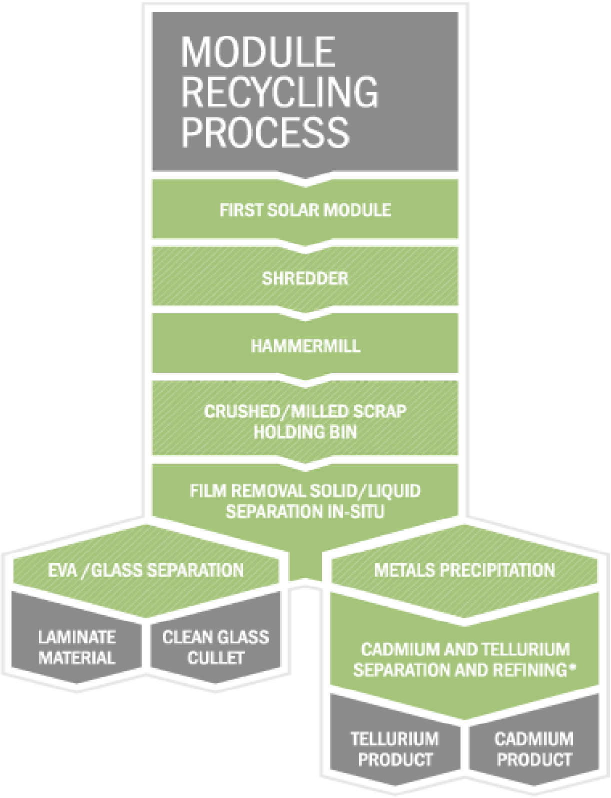


Figure 5 Recycling process of CdTe modules at First Solar

Source: First Solar [7]

2.3.1 PV Cycle

To recycle old modules optimally, a comprehensive system was essential which led to the foundation of the joint initiative association PV Cycle. PV Cycle is a pan-European producer scheme, offering dedicated compliance and waste management services for solar energy system. PV Cycle was founded in 2007 as a volunteer initiative specific to PV module waste. Several European countries are members and new countries are joining with the WEEE directive, which is being fully revamped to include PV module. The organization is headquartered in Brussels and with member countries like UK, Netherlands, France, Czech Republic, Germany, Spain, Switzerland, Belgium, and, Bulgaria. [8]

PV Cycle has enabled its members to comply with local requirements in an easy and effective way. Waste management needs to comply with EU, national and regional legislation namely: WEEE Directive, Waste Framework Directive, Waste Shipment Regulation, and Battery Directive. As each EU nation has its own national and local legislation the PV cycle has enabled harmonization among these legislations to be folded into the 2014 newly revised WEEE Directive. Currently, PV Cycle has four ongoing projects which are listed below.[9]

a. Full Recovery End Life Photovoltaic (FRELP)

The FRELP project aims to test and develop innovative technologies for 100% recycling of end-of-life PV panels in an economically viable way. Two main environmental solutions are proposed the recovery of high quality extra clear glass, to be used in the hollow and flat glass industry, thus implying very significant energy and CO_2 emission savings in the glass melting process. The recovery of (metallic) silicon, to be used as ferrosilicon in iron silicon alloys or, if pure enough, transformed into amorphous silicon to produce thin films, thus greatly reducing energy consumption and CO_2 emissions associated with the production of primary silicon.

b. Cradle-to-cradle sustainable PV modules (CU-PV)

CU-PV is a pan-European R&D project under the European Union's FP7 Programme. With the goal of improving the environmental profile of silicon based PV modules, the CU-PV partners investigate the reduction of silver and lead in PV, ways to eco-design and high-value end-of-life treatment. Bringing research, production and waste treatment partners to this project, CU-PV covers the entire life cycle of a silicon based PV module.

c. ReSolar

Working on optimizing the performance in PV module recycling, ReSolar researches into improved collection and recycling by improving communication and alignment between waste recyclers and material processors. ReSolar is a joint initiative of 10 Belgium companies, research institutes and waste officials and funded by the Flemish Government Agency for Innovation by Science and Technology.

d. CABRISS

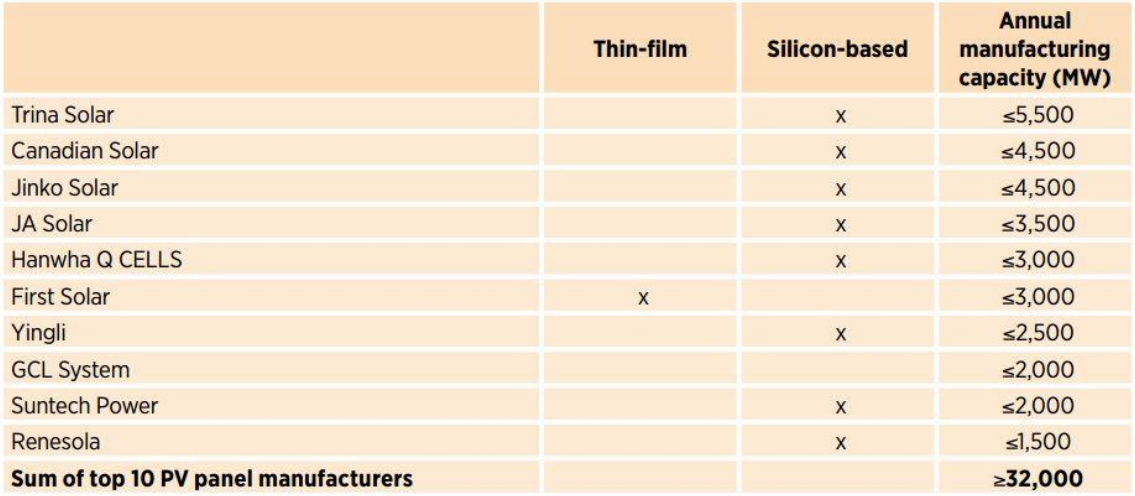
CABRISS stands for implementation of a CirculAr economy Based on Recycled, reused and recovered Indium, Silicon and Silver materials for photovoltaic and other applications. Focusing on the creation of a circular economy by using and re-using recycled waste materials from PV modules and other products, CABRISS is a joint initiative of 16

European companies and research institutes and received approval by the EU’s Horizon 2020 – Research and Innovation Framework Program.

3. METHODOLOGY

3.1 Module Specifications

To get representative results of the photovoltaic (PV) market, a literature study was conducted to identify the major PV module manufacturers, based on their annual manufacturing capacity as shown in Fig. 6. Of these, one crystalline Si manufacturer was randomly selected and a module from a vendor for this manufacturer was purchased to develop the sample extraction procedure and to perform the TCLP testing.



	Thin-film	Silicon-based	Annual manufacturing capacity (MW)
Trina Solar		x	≤5,500
Canadian Solar		x	≤4,500
Jinko Solar		x	≤4,500
JA Solar		x	≤3,500
Hanwha Q CELLS		x	≤3,000
First Solar	x		≤3,000
Yingli		x	≤2,500
GCL System			≤2,000
Suntech Power		x	≤2,000
Renesola		x	≤1,500
Sum of top 10 PV panel manufacturers			**≥32,000**

IRENA/IEA-PVPS estimates, 2016[9]

Figure 6 Major PV manufacturers based on annual manufacturing capacity[1]

Table 1 Module Dimensional Specifications

Weight (kg)	19.1
Length (mm)	1650
Width (mm)	992
Number of cells (mm)	60

3.2 Sample extraction procedure

“Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its 2 narrowest dimension (i.e., can pass through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above." [10]

A systematic extraction of representative samples from various parts of the test module that meets the EPA Method 1311 requirements is described below. Samples are extracted from all three different parts of the module (laminate, frame and junction box with cables & connectors) proportional to their individual weights. The extracted samples from each part is cored and cut to meet the size requirement. To calculate number of samples to be cored from each area of the laminate (cell, non-cell and ribbon), their individual areas are calculated. Their proportional percentage is calculated with respect to the total area and proportional number of samples are cored.

Ideally, based on the weights of each of the components, proportional number of samples are extracted as shown in flowchart below (Fig. 7). However, the number of samples for the JCC is very less and is not a uniform representation of the entire part. If the number of samples in the JCC is increased to make it a uniform representation, then number of samples must be increased proportionally for the laminate. Extracting more than 200 samples is tedious and weakens the laminate, challenging the uniform size coring. These feasibility limitations make it impractical to get the samples. A more practical approach is shown in Fig. 8

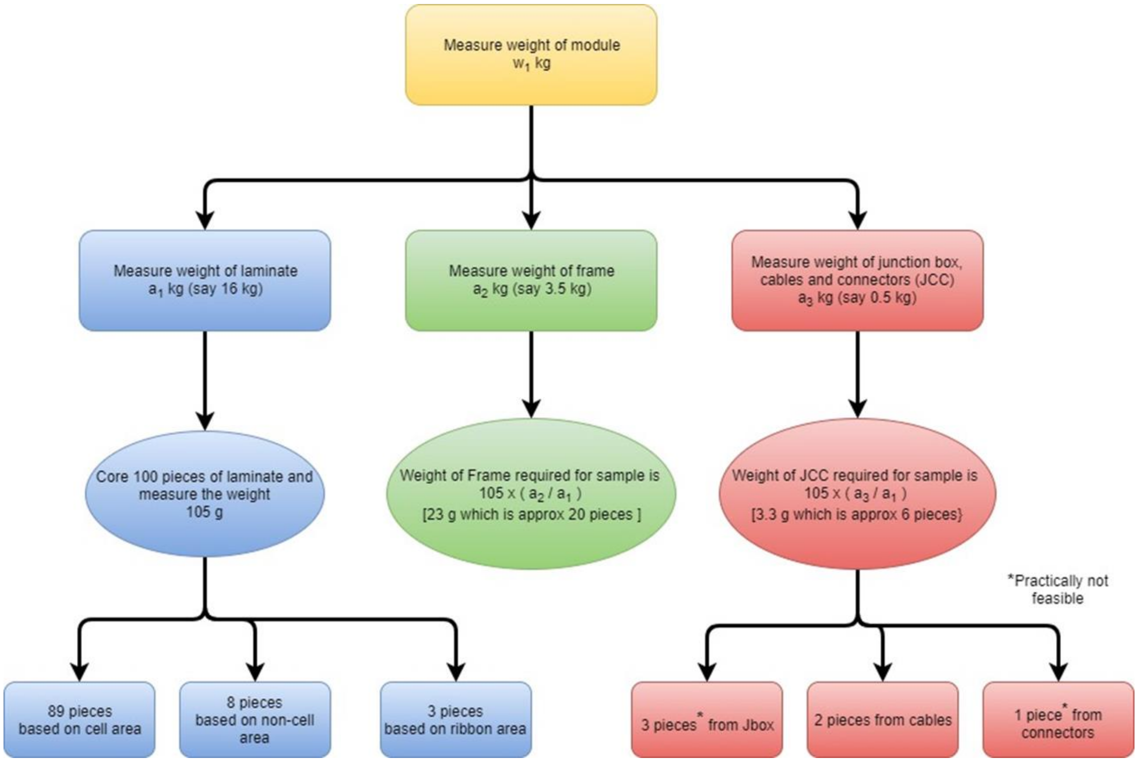


Figure 7 Ideal case approach for sample extraction

To overcome the practical limitations in the ideal case, three parts in the module are identified and 100g of minimum samples are extracted from each part. These samples are extracted to represent the part as accurately and uniformly as possible. After these samples are extracted, packed and sent to the lab for testing, the results from the labs can be used to calculate the representative value for the module. The flowchart described in Fig. 8 describes the calculation process.

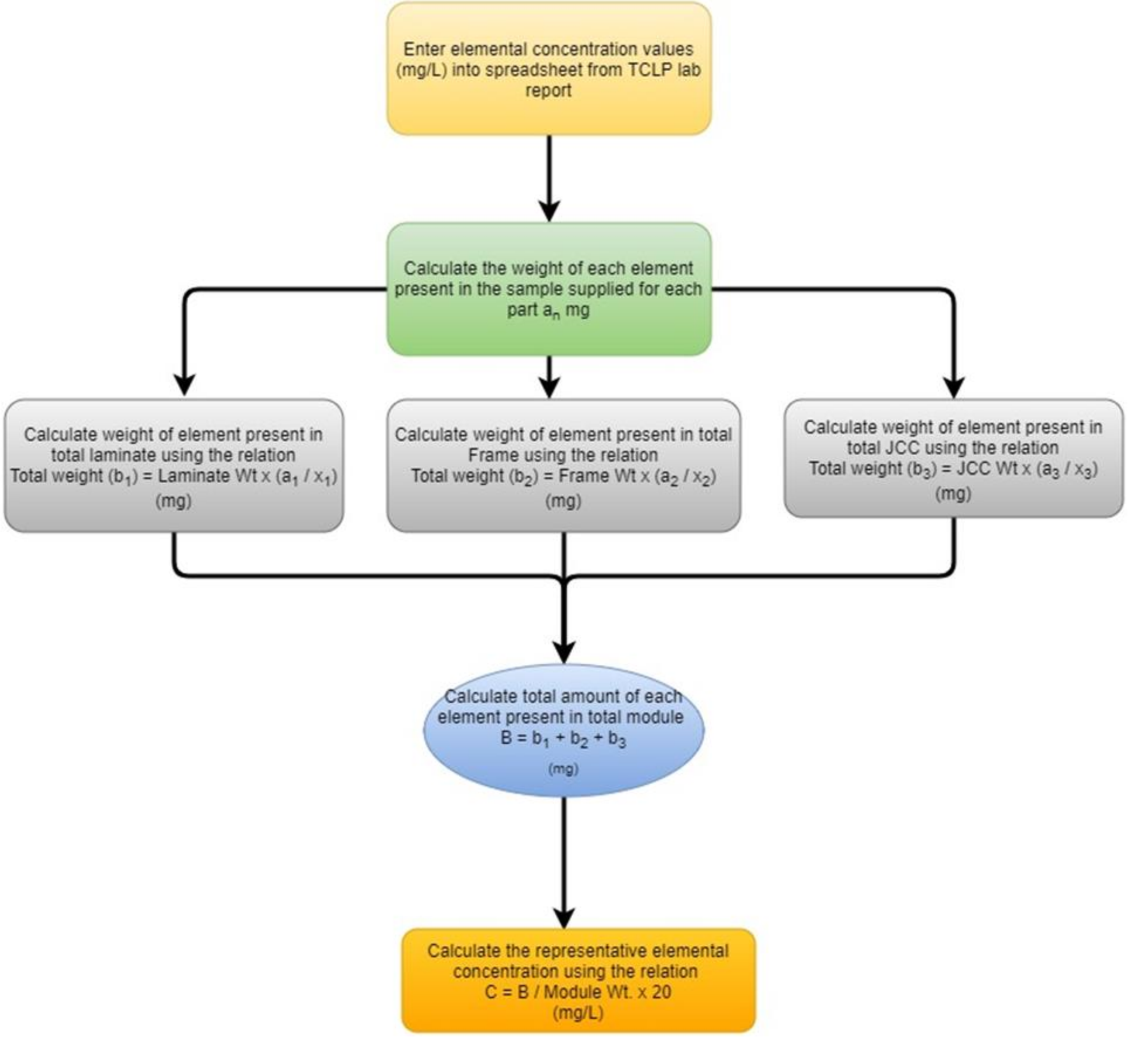


Figure 8 Flowchart describing the calculation of representative value for the entire module

3.2.1 Laminate

First the front and back side of the module is cleaned with water and isopropyl alcohol to remove all impurities including soiling. The soil can contain various minerals and they can provide misleading results. Next, the module is weighed using a spring balance as shown in Fig. 9 to get the module weight (W_1). This can be validated using the name plate data provided in the spec sheet. Since the objective is to take the samples to obtain the representative value of the module, the cell area, non-cell area and ribbon area are measured and the proportional number of pieces to be cored from each area is calculated as shown in Fig. 10.

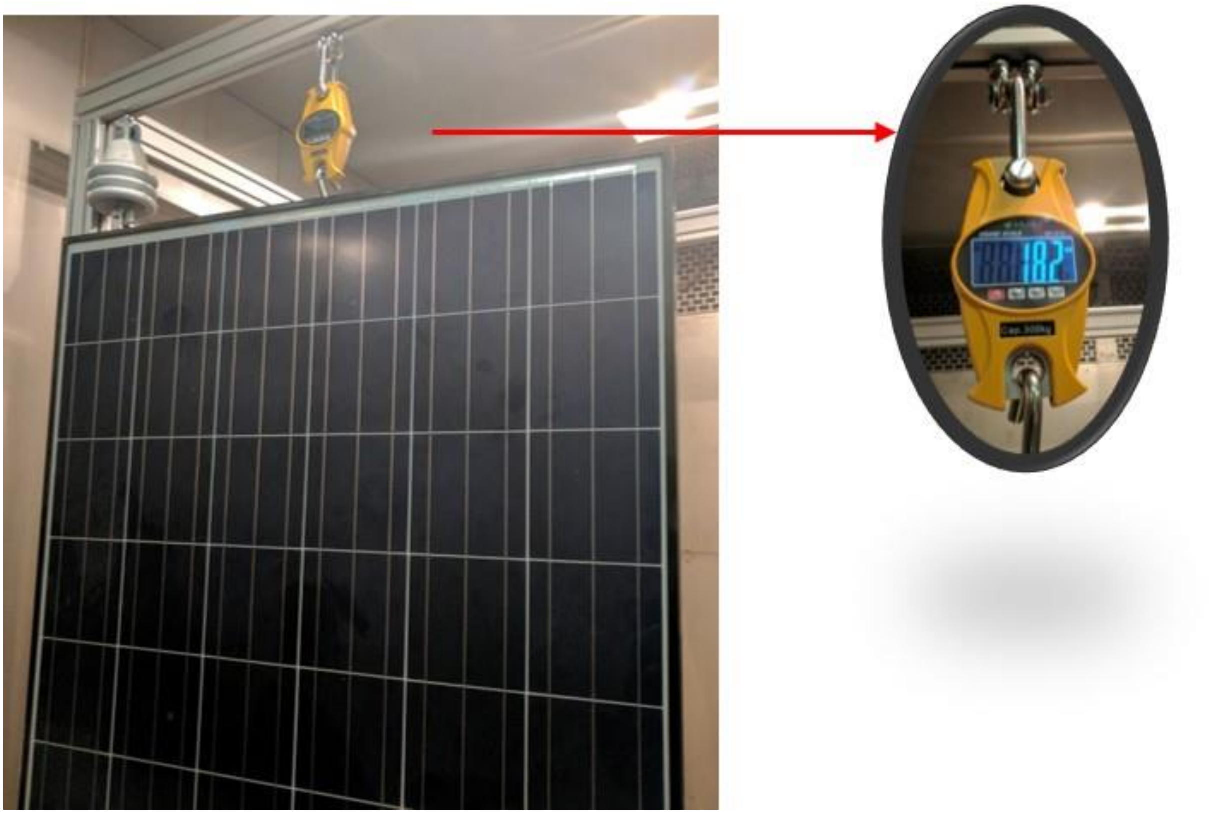


Figure 9 Weighing the module using a spring balance

Using a ½’ coring bit with inner diameter of 9.5 mm (Fig. 11), proportional number of samples from each of the identified areas (in Fig. 10) are cored in the laminate. A sample photograph of a cored laminate is shown in Fig. 12. It must be ensured that the weight of each sample from each of the cored areas is higher than 100g as required by TCLP labs.

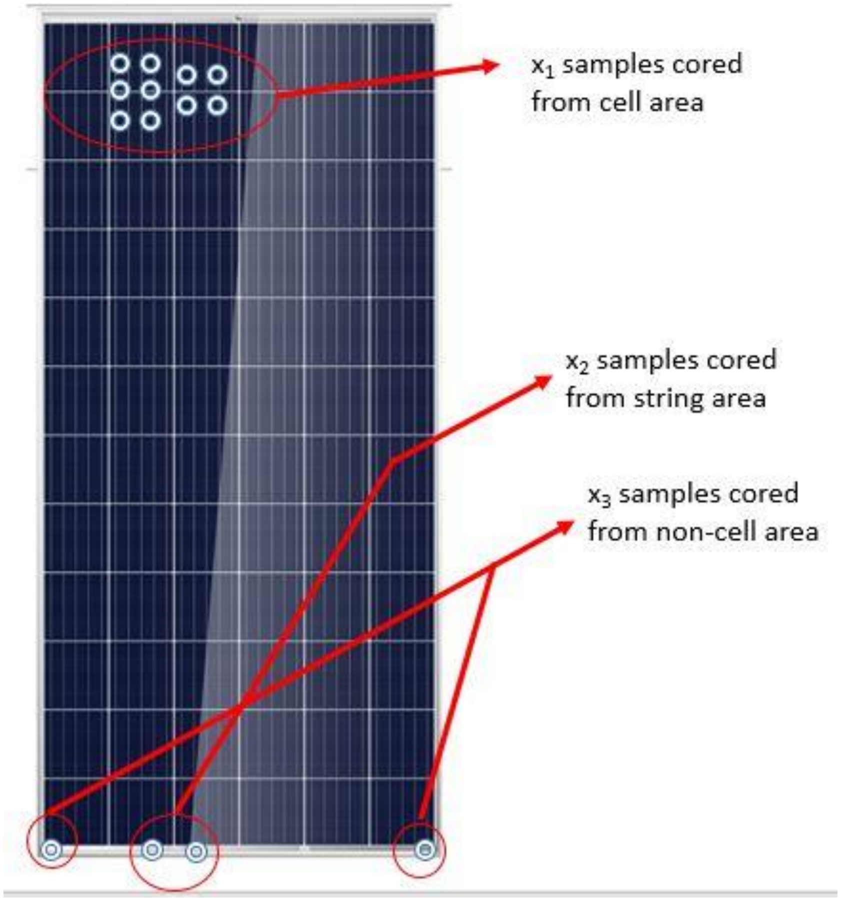


Figure 10 Coring of samples proportionally from different areas in the laminate

Figure 11 Diamond Coring bit used for extracting samples

Figure 12 Sample photograph of a cored laminate

3.2.2 Frame

The frame of the module is generally made up of aluminum. To calculate the weight of the frame, a portion (50-100 mm long) of the frame is cut (Fig. 13) and its length, grove depth is measured. The grove depth is required to accurately calculate the weight of non-cell area portion of the laminate which is hidden inside the grove. This small portion of the frame is then weighed and weight of the piece per unit length (g/mm) is calculated. Using the perimeter of the frame in millimeter (2 x length + 2 x width), and the weight of frame for a known length (for example 100 mm) the total frame weight (W_2) is calculated. Another piece of the frame is extracted from the module and this is cut into smaller pieces (approximately 1 cm^2 area) as shown in Fig. 14. These pieces constitute the samples for the frame and a minimum of 100g of samples is taken.

Table 2 Frame weight calculations

Frame	
Weight of sample (g)	59.42
Density (g/cm)	5.94
Perimeter (mm)	5284
Frame Weight (kg)	3.14

Figure 13 A portion (10 cm length) of frame

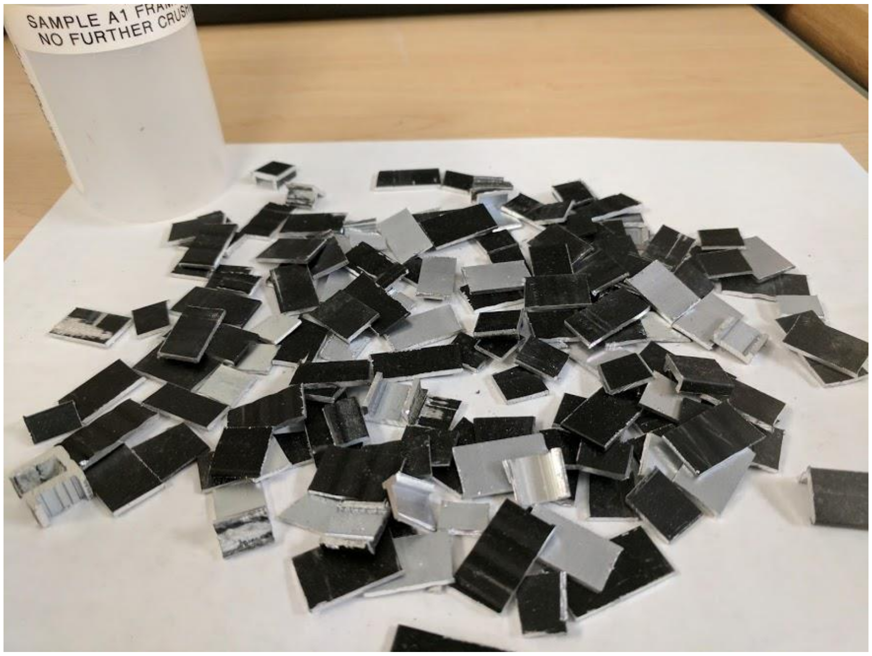


Figure 14 Samples of frame ready for packaging and testing

3.2.3 Junction box, cables and connectors

The third part of the sample to be extracted include the junction box (j-box), cables and the connectors. To remove the cables and connectors, use a wire cutter to snip at the connecting point of the junction, to leave as little cable attached as possible. Similarly, the other ends of each of the cables are snipped to remove the connectors. Now, a portion of the cable of known length (say 15 cm) is cut and weighed, thus obtaining weight per unit length of the cable (g/cm). Using the total length of the cables (2 in number) the total cable weight (W_3) is obtained. The connectors that were snipped are weighed separately to obtain their weight (W_4) as shown in Fig. 15. The cables and connectors are cut into smaller pieces (9.5 mm) and put inside a container. The junction box is now cut along with the laminate, to extract it from the module. Since we know the weight of laminate per sq.cm, and the dimensions of the laminate attached with the junction box, we can calculate the weight of the j-box (W_5). Now the ½' coring bit is used to extract samples from the junction box Fig. 17. It is ensured that the cumulative weight of the samples taken from the junction box, cables and connectors (JCC) is at least 100g.

To obtain the weight of the laminate, we make use of the other individual weights measured and the difference with the module weight.

Weight of laminate $W_6 = W_1 - [W_2 + W_3 + W_4 + W_5]$

Now, each of the extracted samples is packed in specialized containers (Fig. 10) and sent to the TCLP labs instructing them to test each sample individually, i.e. three tests – i) laminate, ii) frame and iii) junction box, cables & connectors (JCC). The samples must be used as is without needing further crushing.

Figure 15 Connectors removed from cables and J-box to be weighed

Figure 16 Cables removed from J-box to be weighed

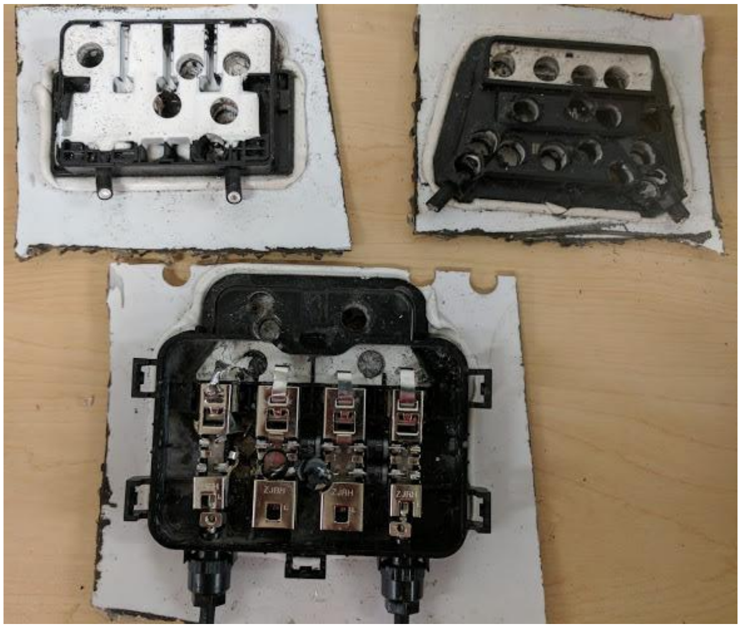


Figure 17 J-box of different modules cored to extract samples

3.3 Sample extraction setup

For extracting samples from the laminate, a diamond coring drill is used. The CRL AMZ1 Production Diamond Drilling Machine (Fig. 18) drills 1/8" to 4" (3 to 102 mm) holes faster and more precisely than any other portable glass drilling machine. Per Method 1311 of EPA, the sample size can be a maximum of 9.5 mm.[10] So, a ½" Belgian thread, diamond coring bit is used to extract samples. The specifications of the drilling machine are given below.

- Variable Speed, High Torque D.C. Motor
- Electronic Variable Speed Control ranging from 0 to 2900 RPM
- Locking Vacuum Cup Base
- Built-In Handle for Easy Carrying
- 12' (3.6 m) Heavy-Duty Power Cord

- Height - 16 in (406.4 mm)
- Weight – 48 lb. (21.77 kg)

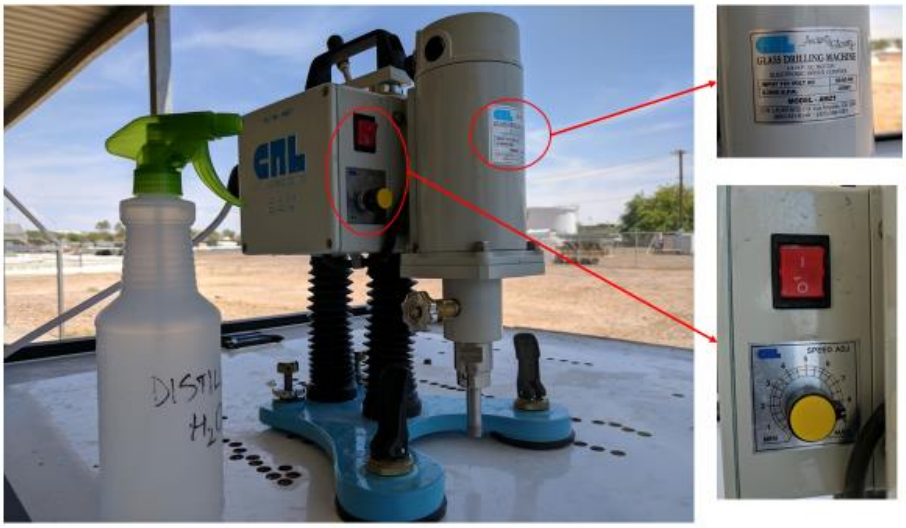


Figure 18 CRL Glass coring machine with diamond coring bit

For extracting the samples, it is preferred to core the module from the rear side. The holes are cleaner and material wastage is relatively less. Speed is set at 850 – 900 RPM and water is sprayed externally while coring, as the bit and the glass tend to heat up.

3.4 Particle size determination using Image processing

The Method 1311 of EPA requires the size of the sample to be a maximum of 9.5 mm or surface area per gram of material equal to or greater than 3.1 cm^2.[10] Since the density of the laminate pieces (glass, encapsulant and cell) is much higher than paper, cloth etc., the surface area criteria is not a practical method of measuring the particle size. To present objective evidence, an image processing technique is used to determine average particle size in a broken module. MATLAB is used as the platform for image processing. An initial program was generated using images taken of a few cells in a broken module. The fingers in the cells were of similar intensity as the cracks and hence, the detection of the particles was not very accurate.

3.4.1 Imaging using fluorescent dyes

To minimize the interference of the fingers in the detection of the particles, a fluorescent dye is (Zyglo® ZL-27A Post Emulsifiable Fluorescent Penetrant) was used. This fluoresces a bright greenish-yellow under ultraviolet radiation (UV) with peak wavelength of 365 nm. This is available in the form of an aerosol spray. First the area to be inspected is cleaned with water and rubbing alcohol. It is important to do the precleaning thoroughly to ensure the cracks are open to the surface. Then the penetrant is sprayed on the cracked module as shown in Fig. 19.

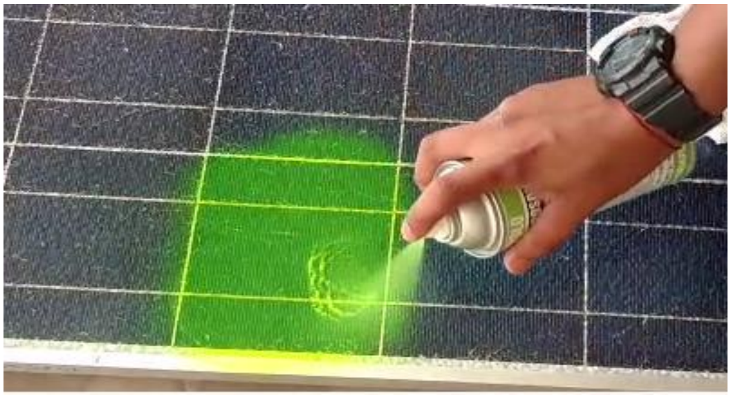


Figure 19 Applying Zyglo Purc, penetrant on area to be inspected

It is a low viscosity, high penetrant oil which can penetrate the cracks. The dye requires a dwell time of about 15 – 30 minutes to penetrate the cracks. After the dwell time, the module is rinsed gently with to remove any excess penetrant on the surface without removing the penetrant in the cracks. This module is then inspected with UV light, and the cracks with the fluorescent penetrant were photographed. These images are then processed and extracted in MATLAB to detect the cracks using the green channel. Despite this, the fingers were bright and could not be distinguished from the cracks thereby making the detection of cracks difficult.

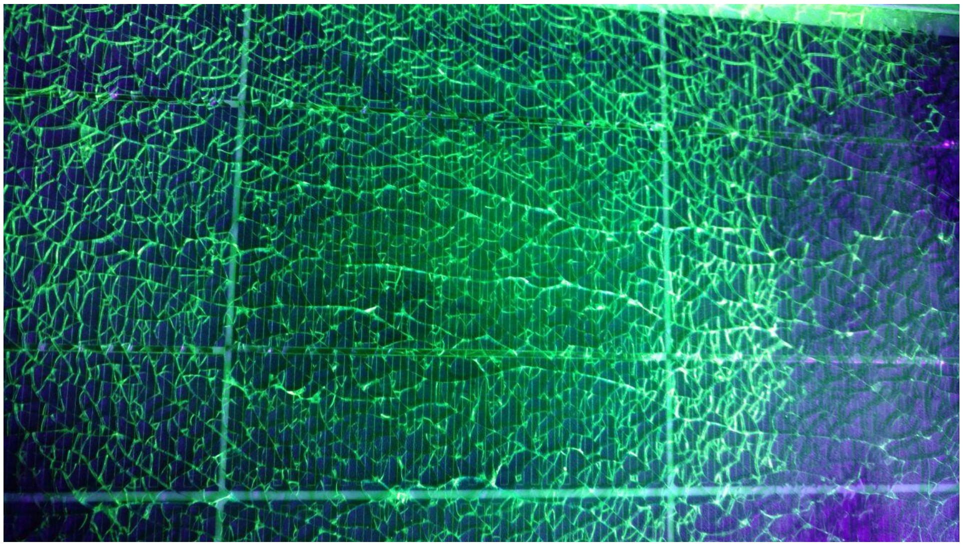


Figure 20 Module with Fluorescent dye inspected in UV light

To solve this issue, the cracks are manually traced and then these modified images are used for the image processing. To make the tracing more accurate, a mask (2 inch x 2 inch) Fig. 21 is made and used on four random spots identified on the module and images are taken. Tracing of this smaller known area is easier and more accurate. Then these images are processed and the average size of the particles is calculated. Knowing the area of the image is useful to determine the area in mm^2, as MATLAB gives the result in pixels.

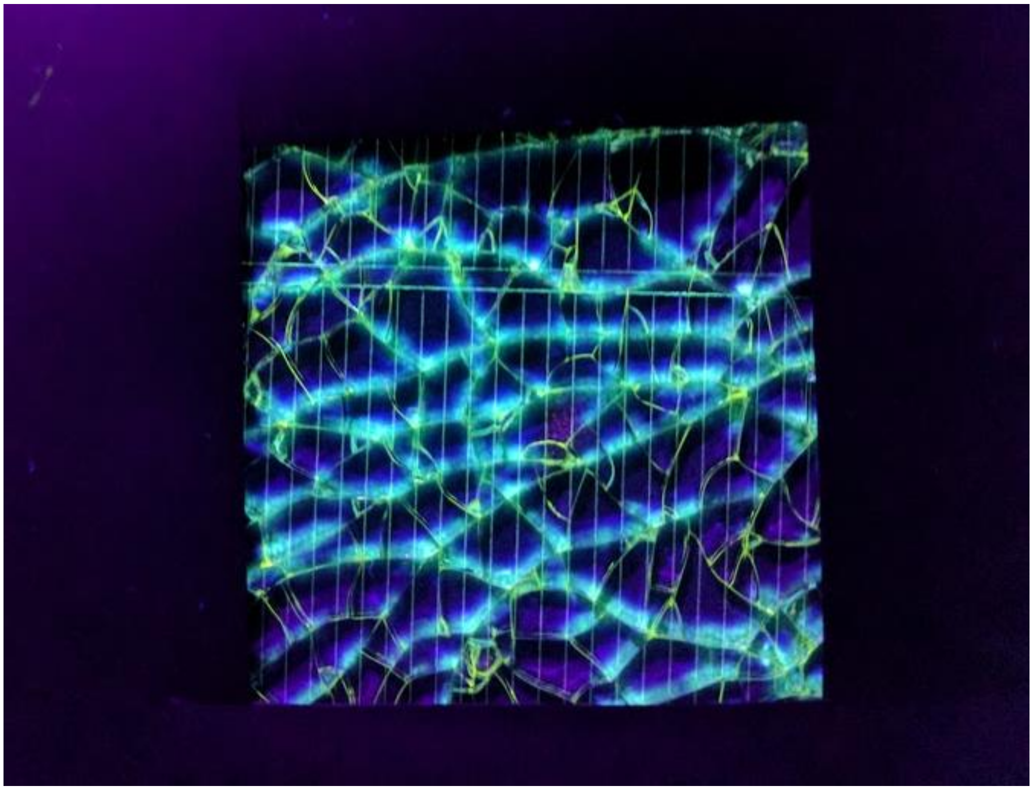


Figure 21 Photograph after using a 2" x 2" mask on the module

3.4.2 Particle size distribution determination

To trace the cracks in the modules, MS Paint is used. In some of the images, that are not taken parallel to the module, double lines appear in the photos for a single crack due to reflection. To accommodate for this, while tracing, it is corrected by drawing a single line, which is average of the two lines. After tracing, only the outline of the cracks was retained to make the processing easy.

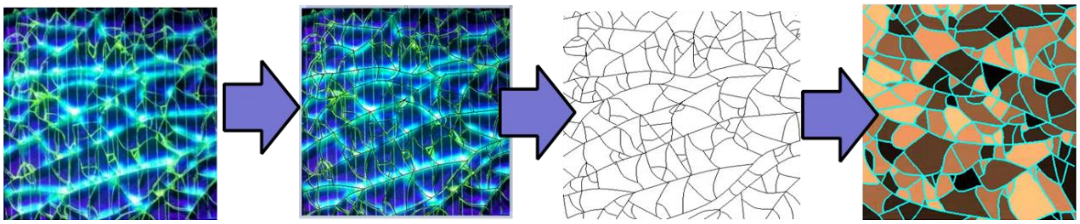


Figure 22 (a) Original image (b) Image with cracks traced (c) Outline of cracks (d) Image with distinct areas identified

The traced image is converted into a binary (Black and White) image for further processing. "*bwconncomp*" function is used to find connected components in the binary image which works on a principle like edge detection. This is followed by the function "*labelmatrix*", which creates label matrix from connected components structure returned by *bwconncomp*. This allows us to identify different, distinct glass pieces, label them and assign a unique color to each glass pieces for simple distinction. The pixels labeled 1 make up one object; the pixels labeled 2 make up a second object; and so on. The number of such labels returns the number of pieces identified. Finally, after the number of the glass pieces is determined, the number of pixels inside each identified piece is counted. This gives the area of each piece in pixels, and using the conversion factor the area in mm^2 is calculated. The conversion factor is adjusted for each image since the number of pixels differs. Pieces identified with pixel count below a certain threshold, (say 15), are not considered for the analysis as it too small and can be neglected. Data that can be obtained using the code are:

1. Number of glass pieces
2. Area of each glass piece
3. Largest, smallest and average area
4. Histogram with size distribution for each image

3.5 TCLP Testing

The EPA Method 1311 – Toxicity Characteristic Leaching Procedure (TCLP) is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. If an analysis of extract obtained shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is determined to be hazardous. The TC.L.P. involves crushing a sample to a particle size of less than 9.5 mm, adding an extraction fluid at a 20-to-l fluid to-sample ratio, and rotating the sample in extraction fluid for 18 hours. One liter of the T.C.L.P. extraction fluid consists of 5.7 mL glacial acetic acid, 64.3 mL 1 N sodium hydroxide, and 930 mL of reagent water. The pH of the extraction fluid is 4.93 ± 0.05. Elements regulated by the TC.L.P. include arsenic, barium, cadmium, lead, mercury, selenium, and silver. [10] This thesis work deals with only sample extraction from the module but not the TCLP testing. The TCLP testing was done by an independent test lab located in the United States.

3.5.1 Packaging of extracted samples

A ½” coring bit is used to extract the samples from different areas of the module, weighed and packed in specialized containers. The containers must be clean and free of any impurities to avoid any contamination of the samples. These containers are labeled clearly with instructions not to be crushed further.

Figure 23 Specialized containers for packaging extracted samples

Table 3 Weight of sample supplied to the TCLP lab

Weight of sample supplied (kg)	
Laminate	0.105
Frame	0.099
JCC	0.099

Table 4 Weigh of components in JCC

JCC Components (g)	
Junction box	58.87
Cables	34.14
Connectors	6.99

3.5.2 TCLP Testing of samples at selected lab

The test lab performed TCLP on the supplied samples without crushing them further. The details of the parts and their weights for different modules are given below.

Table 5 Sample weights of different parts supplied to labs

Part	**Weight of sample supplied to Lab 1 (g)**
Frame	100
Laminate	107
Jbox, Cables and Connectors	99

The TCLP results of each of the three parts for each module is reported by the test lab. These numbers do not indicate a representative value for the module. To obtain a representative value, these numbers are plugged into an excel sheet, where their respective weights are accounted for and factored to calculate the representative value. This value is compared with the regulatory limit to determine if the module is hazardous or not.

4. RESULTS AND DISCUSSIONS

The calculation to determine the amount (mg/L) of toxic elements in the entire module based on the results received from the TCLP lab, the known individual weights of the representative samples supplied and the total weight of the module is discussed in this section. The test results from the TCLP lab is consolidated and plugged into a spreadsheet. The spreadsheet will consider the contribution of each of the sample, and calculate the amount of each element in the analyte present in each individual part as well as the entire module.

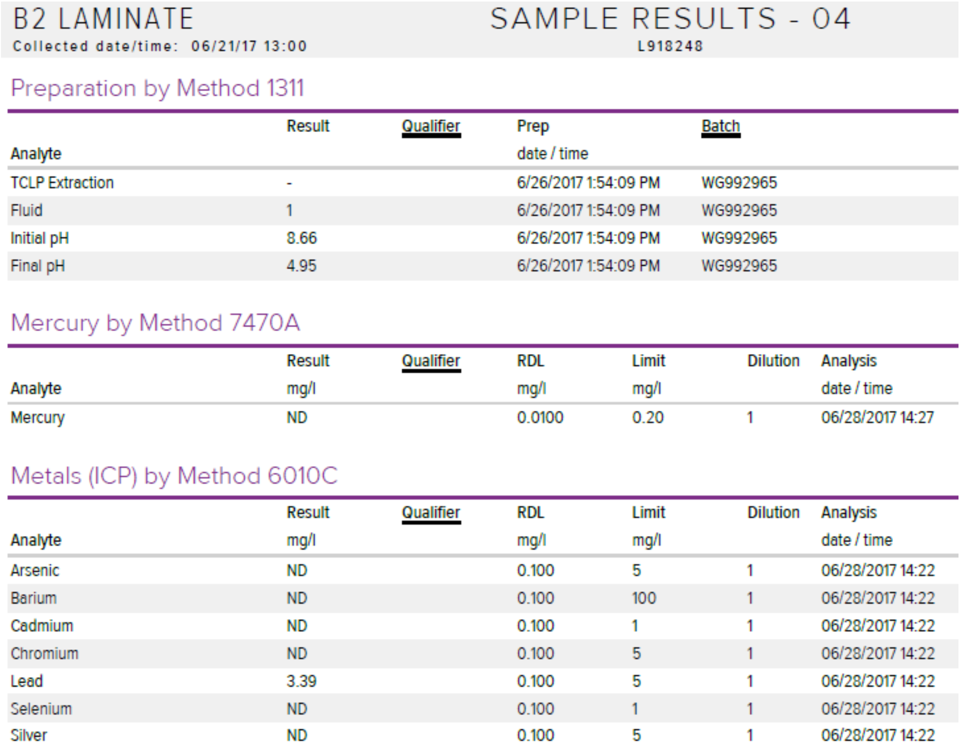
4.1 TCLP results for individual parts

The samples are sent to the lab, with instructions not to crush them any further. The EPA limit for each metal for the TCLP tests is shown in Table 4. The results from the TCLP lab for individual parts is given below. (Table 5-7)

Table 6 EPA limit for different metals

Metal	Limit (mg/L)
Hg	0.2
As	5
Ba	100
Cd	1
Cr	5
Pb	5
Se	1
Ag	5

Table 7 TCLP Lab results for Laminate



B2 LAMINATE
Collected date/time: 06/21/17 13:00

SAMPLE RESULTS - 04
L918248

Preparation by Method 1311

Analyte	Result	Qualifier	Prep date / time	Batch
TCLP Extraction	-		6/26/2017 1:54:09 PM	WG992965
Fluid	1		6/26/2017 1:54:09 PM	WG992965
Initial pH	8.66		6/26/2017 1:54:09 PM	WG992965
Final pH	4.95		6/26/2017 1:54:09 PM	WG992965

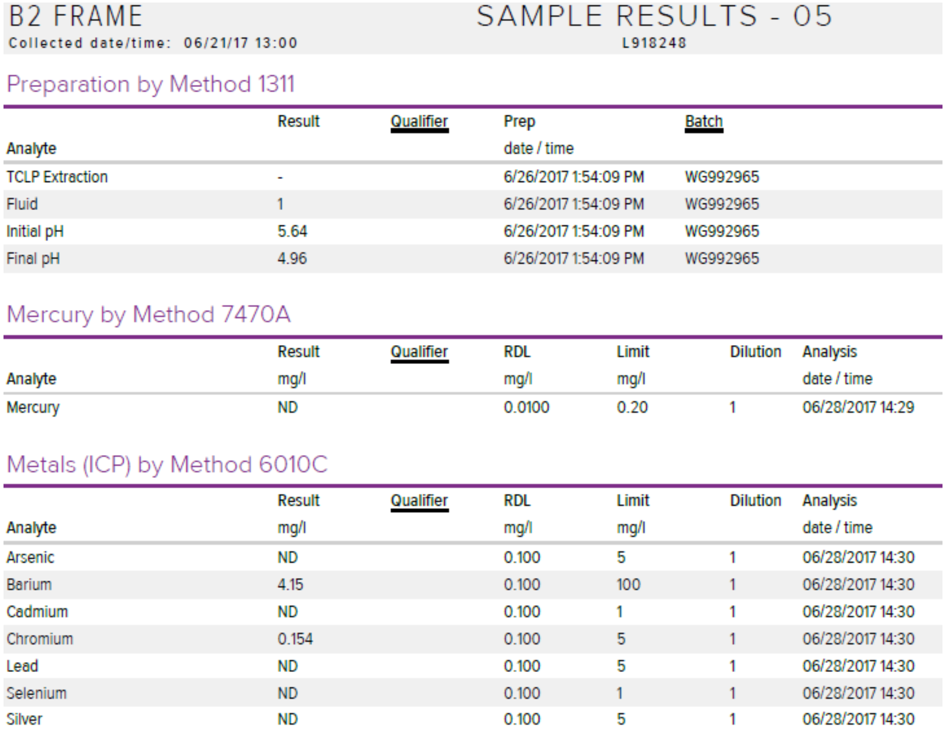
Mercury by Method 7470A

Analyte	Result mg/l	Qualifier	RDL mg/l	Limit mg/l	Dilution	Analysis date / time
Mercury	ND		0.0100	0.20	1	06/28/2017 14:27

Metals (ICP) by Method 6010C

Analyte	Result mg/l	Qualifier	RDL mg/l	Limit mg/l	Dilution	Analysis date / time
Arsenic	ND		0.100	5	1	06/28/2017 14:22
Barium	ND		0.100	100	1	06/28/2017 14:22
Cadmium	ND		0.100	1	1	06/28/2017 14:22
Chromium	ND		0.100	5	1	06/28/2017 14:22
Lead	3.39		0.100	5	1	06/28/2017 14:22
Selenium	ND		0.100	1	1	06/28/2017 14:22
Silver	ND		0.100	5	1	06/28/2017 14:22

Table 8 TCLP Lab results for Frame



B2 FRAME
Collected date/time: 06/21/17 13:00

SAMPLE RESULTS - 05
L918248

Preparation by Method 1311

Analyte	Result	Qualifier	Prep date / time	Batch
TCLP Extraction	-		6/26/2017 1:54:09 PM	WG992965
Fluid	1		6/26/2017 1:54:09 PM	WG992965
Initial pH	5.64		6/26/2017 1:54:09 PM	WG992965
Final pH	4.96		6/26/2017 1:54:09 PM	WG992965

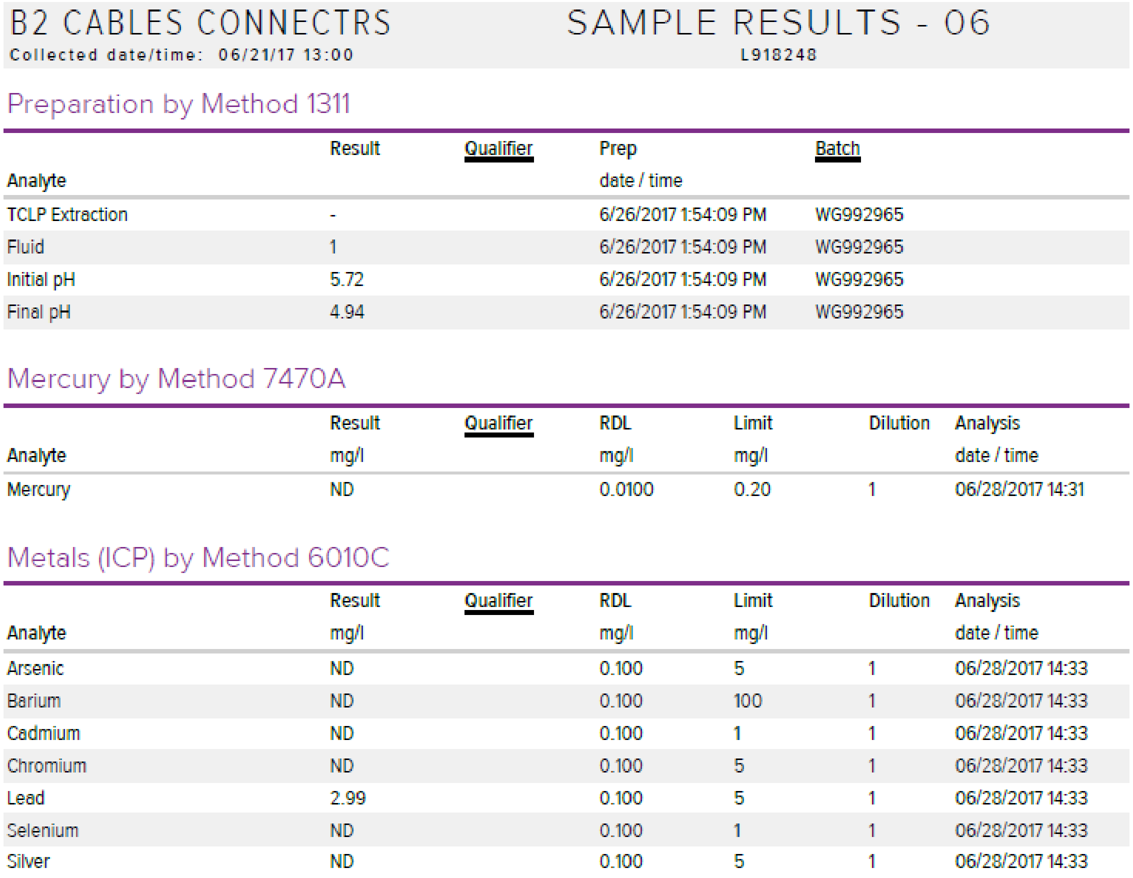
Mercury by Method 7470A

Analyte	Result mg/l	Qualifier	RDL mg/l	Limit mg/l	Dilution	Analysis date / time
Mercury	ND		0.0100	0.20	1	06/28/2017 14:29

Metals (ICP) by Method 6010C

Analyte	Result mg/l	Qualifier	RDL mg/l	Limit mg/l	Dilution	Analysis date / time
Arsenic	ND		0.100	5	1	06/28/2017 14:30
Barium	4.15		0.100	100	1	06/28/2017 14:30
Cadmium	ND		0.100	1	1	06/28/2017 14:30
Chromium	0.154		0.100	5	1	06/28/2017 14:30
Lead	ND		0.100	5	1	06/28/2017 14:30
Selenium	ND		0.100	1	1	06/28/2017 14:30
Silver	ND		0.100	5	1	06/28/2017 14:30

Table 9 TCLP Lab results for J-box, cables and connectors (JCC)



B2 CABLES CONNECTRS SAMPLE RESULTS - 06

Collected date/time: 06/21/17 13:00 L918248

Preparation by Method 1311

Analyte	Result	Qualifier	Prep date / time	Batch
TCLP Extraction	-		6/26/2017 1:54:09 PM	WG992965
Fluid	1		6/26/2017 1:54:09 PM	WG992965
Initial pH	5.72		6/26/2017 1:54:09 PM	WG992965
Final pH	4.94		6/26/2017 1:54:09 PM	WG992965

Mercury by Method 7470A

Analyte	Result mg/l	Qualifier	RDL mg/l	Limit mg/l	Dilution	Analysis date / time
Mercury	ND		0.0100	0.20	1	06/28/2017 14:31

Metals (ICP) by Method 6010C

Analyte	Result mg/l	Qualifier	RDL mg/l	Limit mg/l	Dilution	Analysis date / time
Arsenic	ND		0.100	5	1	06/28/2017 14:33
Barium	ND		0.100	100	1	06/28/2017 14:33
Cadmium	ND		0.100	1	1	06/28/2017 14:33
Chromium	ND		0.100	5	1	06/28/2017 14:33
Lead	2.99		0.100	5	1	06/28/2017 14:33
Selenium	ND		0.100	1	1	06/28/2017 14:33
Silver	ND		0.100	5	1	06/28/2017 14:33

4.2 TCLP results for representative module

The results from the TCLP lab for individual parts is used to calculate the elemental concentration present in the module. From the results, it is evident that the only harmful element detected is lead, (Pb). This is detected in the laminate as well as JCC. To ensure that this value is representative of the module, the weight of each element present in the entire module is calculated. The TCLP labs report the amount of each element in terms of concentration, i.e mg of analyte per liter (mg/L). This is converted into weight by taking in account of the amount of extraction fluid used. Per the EPA Method 1311, the amount of extraction fluid is 20 times the solid phase and this conversion factor is used to calculate the weight of each element for individual parts. Using the ratio of the weight of laminate with the weight of the entire module, and the amount of solvent that would have been used for the entire module (20 x module weight), the representative value is calculated for the module. The flowchart below (Fig. 24) explains the procedure clearly.

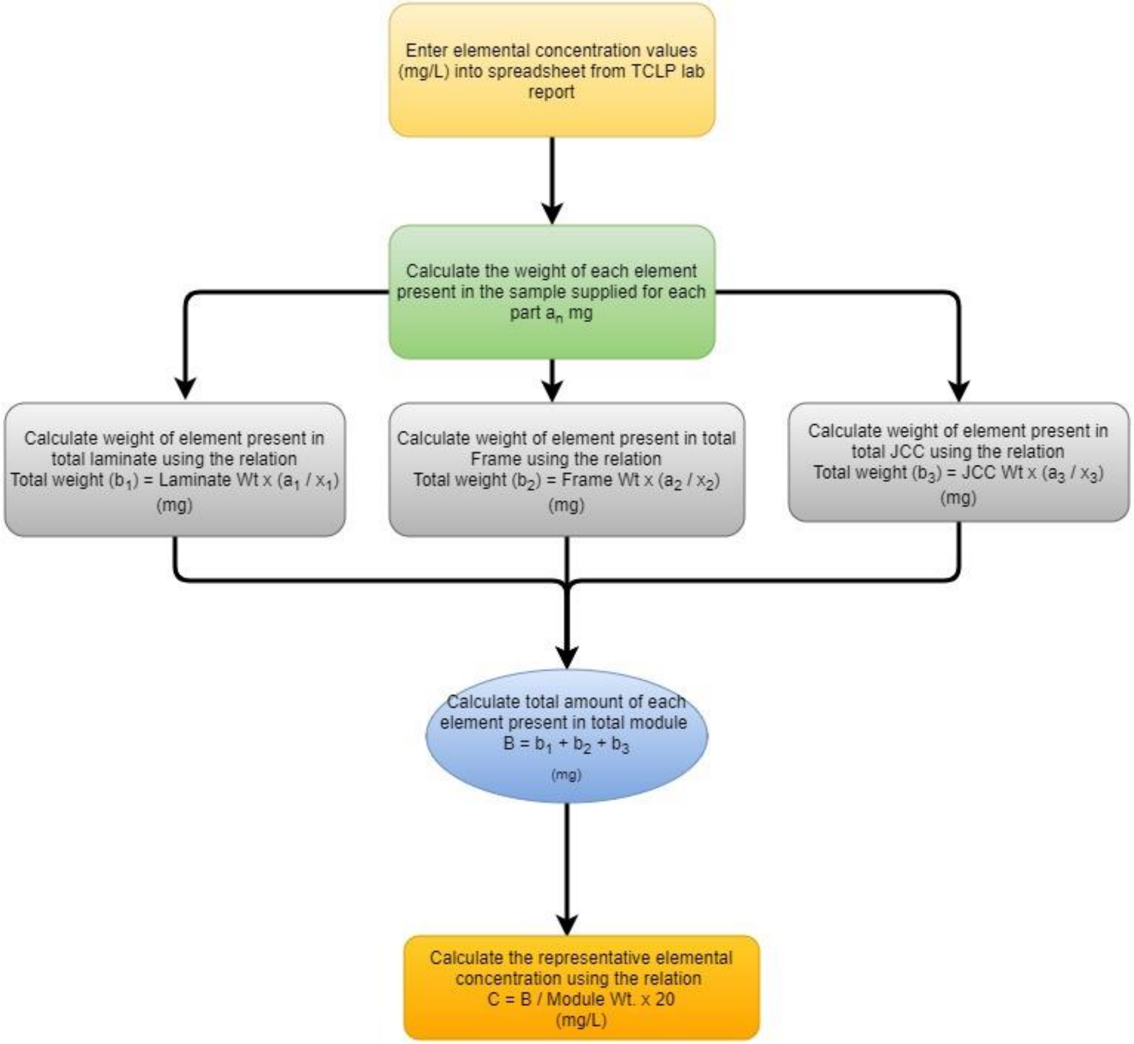


Figure 24 Flowchart describing the calculation of representative value for the entire module

Table 10 TCLP results for entire module

	Weight of sample supplied	Pb (mg/L)	As (mg/L)	Ba (mg/L)	Cd (mg/L)	Cr (mg/L)	Se (mg/L)	Ag (mg/L)	Hg (mg/L)
Laminate	0.105	3.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Frame	0.099	0.00	0.00	4.15	0.00	0.15	0.00	0.00	0.00
JCC	0.099	2.99	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Amount in total laminate sample provided (mg)		7.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Amount in total frame sample provided (mg)		0.00	0.00	8.22	0.00	0.30	0.00	0.00	0.00
Amount in total JCC sample provided (mg)		5.92	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total amount in entire sample		13.04	0.00	8.22	0.00	0.30	0.00	0.00	0.00
Weight of module (kg)	19.1								
Amount in total module (mg/L)		2.82	0.00	0.68	0.00	0.03	0.00	0.00	0.00

4.3 Summary analysis on meeting EPA 1311 regulation

The EPA Method 1311 requires the maximum particle size to be 9.5mm or a surface area per gram greater than or equal to 3.1cm^2 for performing TCLP tests. To validate this number, a new image processing technique is used to determine the average particle size in a broken module. The image processing algorithm, developed at ASU PRL, detects and counts individual glass pieces and measures its area. The area of each piece gives a measure of the particle size. Four different images from different spots in the module were chosen and the results are discussed below.

The particle size distribution for the four spots chosen are shown in Fig. 25 – 28. It is seen that most of the particles are within 0-10 mm^2 range. The average size of the particle is approximately 1 cm^2. The average weight of the laminate, per cm^2 is much higher than 1 g and this is measured by weighing the cored samples. The diameter of the samples is known and its surface area can be calculated. Since the density is much higher than the requirement, further particle size reduction is not necessary.

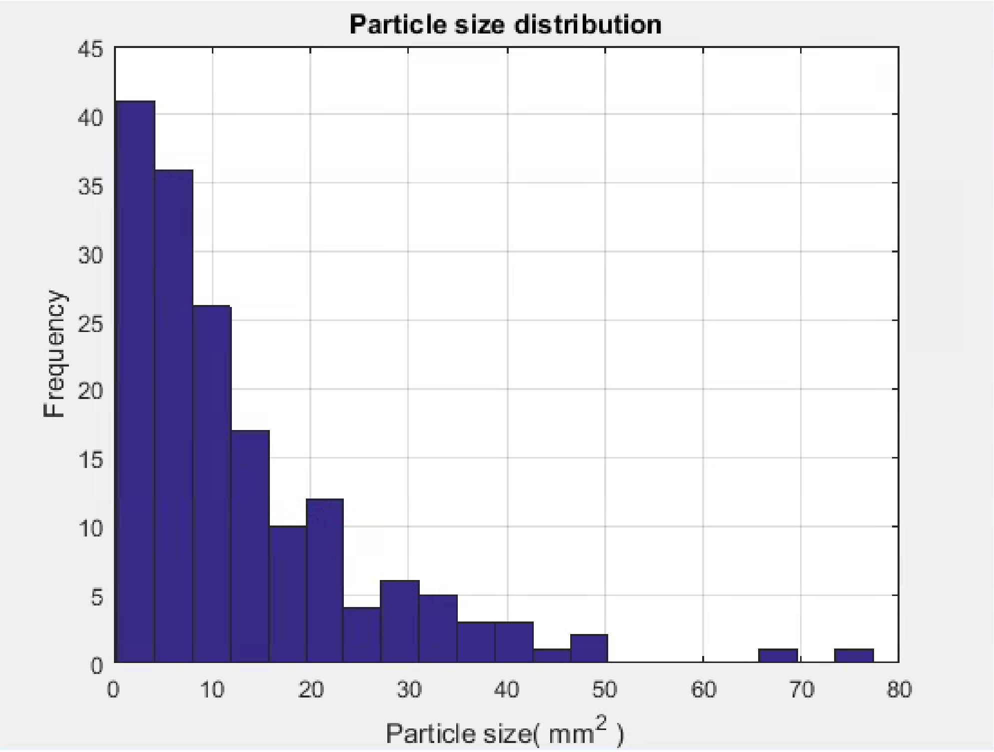


Figure 25 Particle size distribution for Image 1

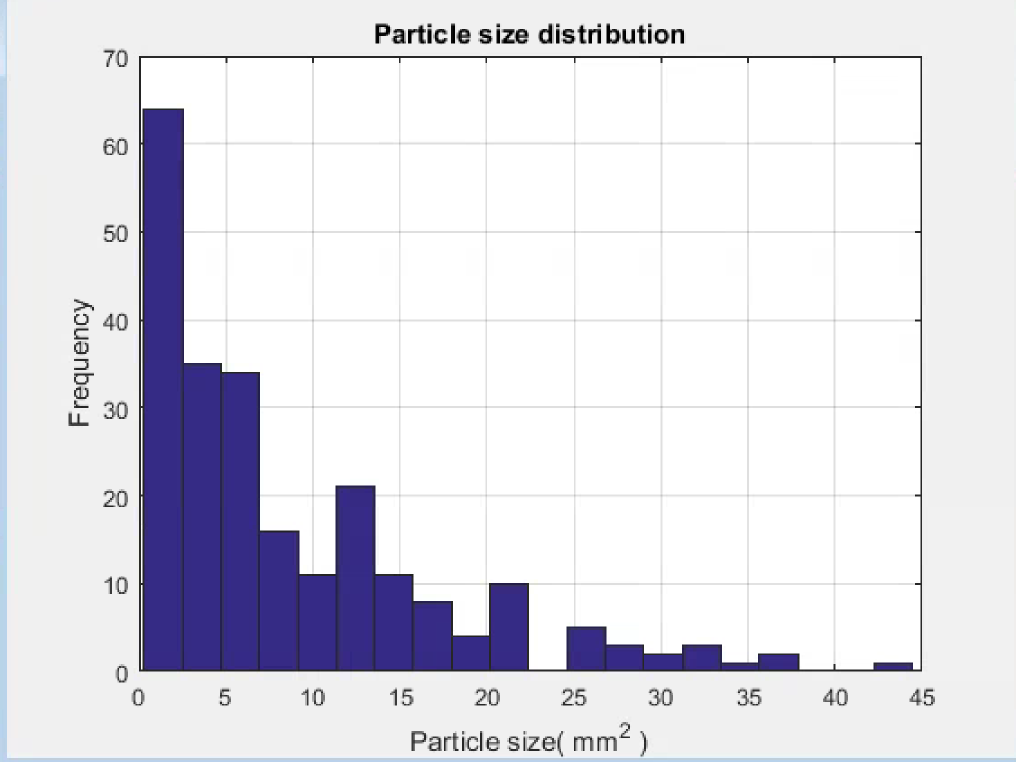


Figure 26 Particle size distribution for Image 2

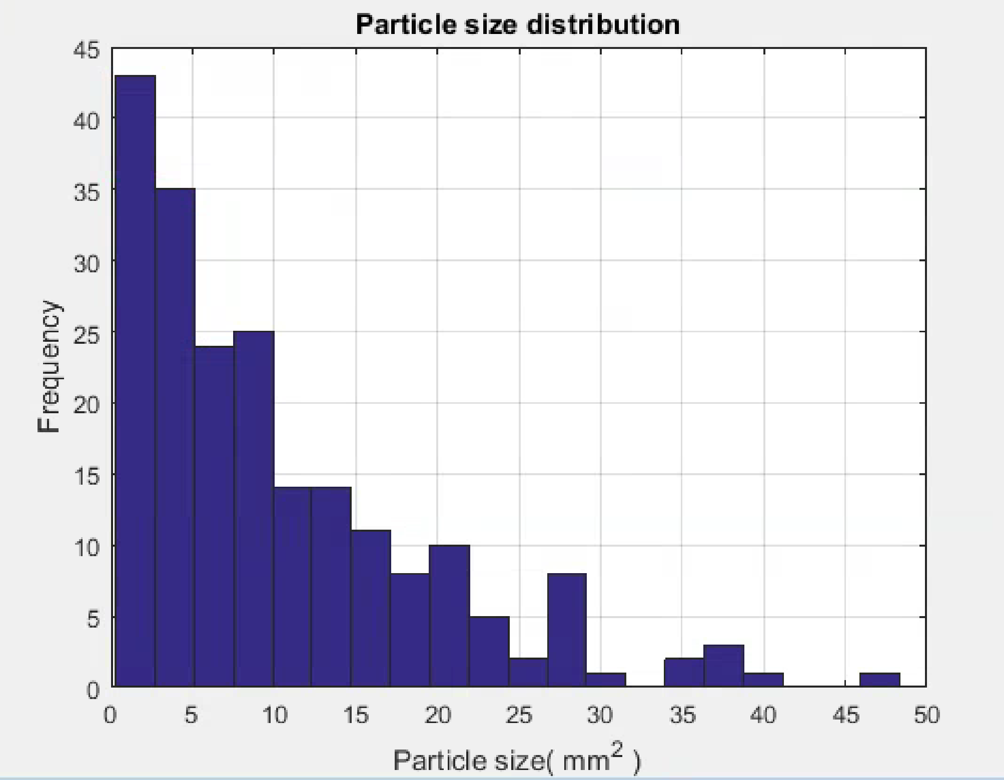


Figure 27 Particle size distribution for Image 3

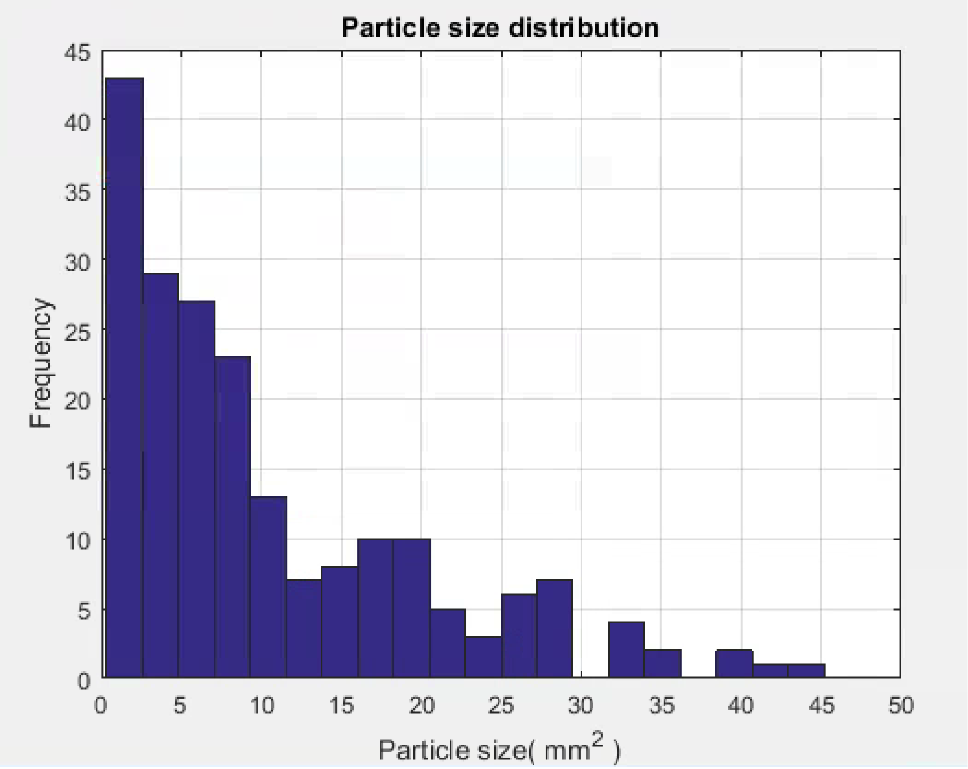


Figure 28 Particle size distribution for Image 4

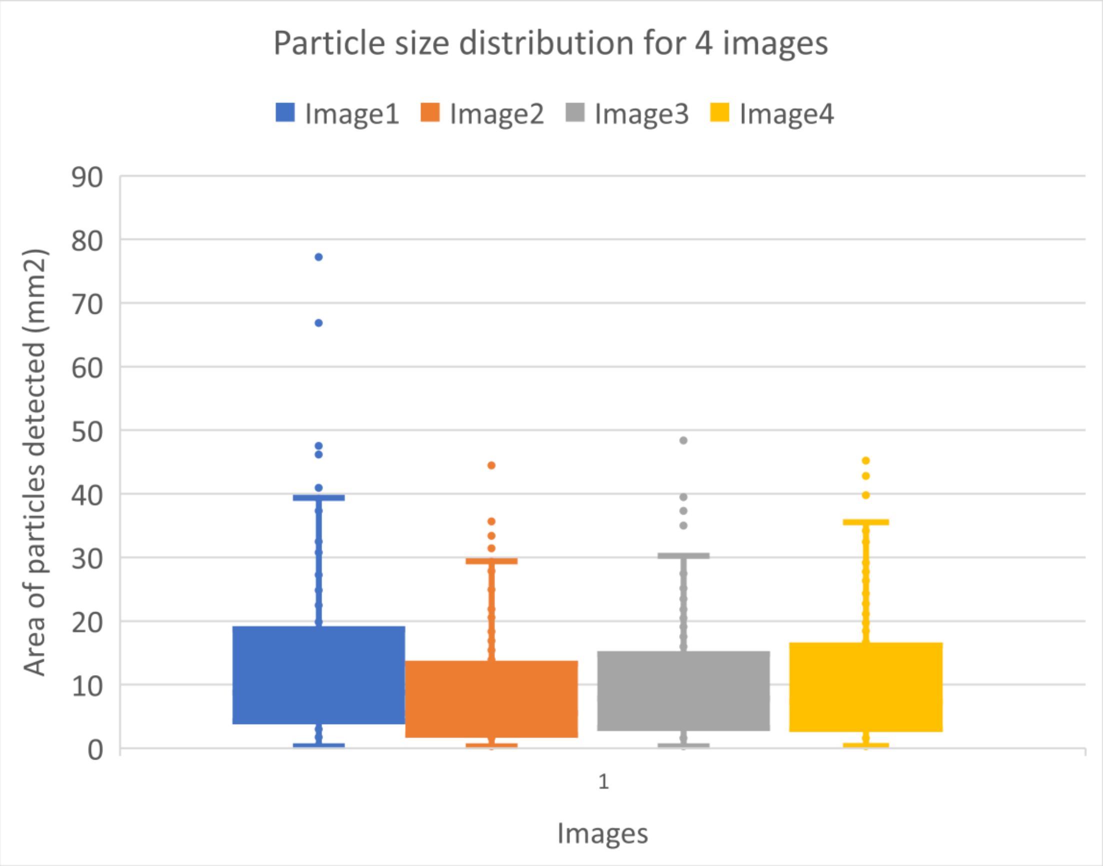


Figure 29 Comparison of area of particle sizes in 4 images using the image processing algorithm

Table 11 Minimum, maximum and average particle sizes detected by the image processing algorithm

	Min area(mm2)	Max area(mm2)	Average area(mm2)	No. of glass pieces
Image 1	0.31114	77.2362	12.7748	168
Image 2	0.28672	44.4777	8.6599	231
Image 3	0.30269	48.3673	10.26	207
Image 4	0.33452	45.1914	10.598	201

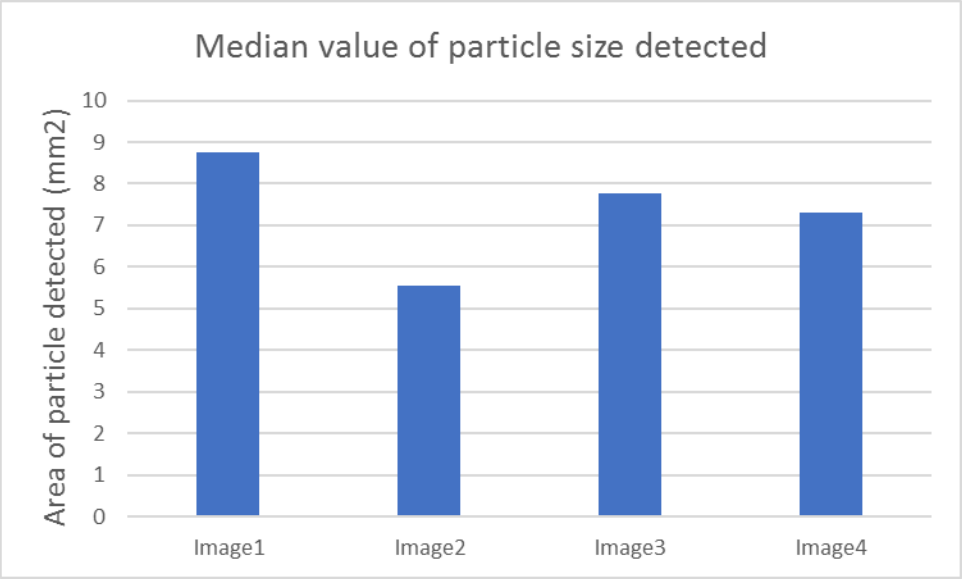


Figure 30 Median value of detected particle

5. CONCLUSION

With the rising cost of electricity and advancement in solar PV technology, there will be an increase for the demand of solar PV technology within the residential and commercial markets. In 20 to 25 years these panels will reach their end-of-life and the cumulative amount of PV waste will force the solar industry to be more conscious about developing an environmentally sustainable and cost effective method of disposing this industrial waste. Nonetheless, some solar manufacturing companies have begun to voluntarily recycle solar modules, but such initiatives are driven by environmental responsibility rather than economic benefit. Therefore, as PV waste appears 25-30 years after the module is created and the PV industry is experiencing explosive growth, there will be increased need to recycle the large amount of decommissioned solar modules. Because recycling is currently economically unfavorable, this will ultimately lead to economic stress on voluntary initiatives. Consequently, unless recycling of solar modules is regulated in the future, it is likely that these types of voluntary initiatives will not be sustainable and hazardous materials may begin entering local waste streams.

5.1 Sample extraction methodology

The sample extraction may seem to be a very straightforward and simple procedure. After experimenting with a lot of different coring techniques and different machines, the CRL AMZ1 diamond drilling machine is chosen. It produces high precision and clean cuts with minimal material wastage. This is validated by the fact that 142 sample pieces extracted in a previous experiment weighed 110 g while 89 pieces extracted with the CRL drilling machine, weighed 94 g as expected. The other advantage of this machine is, it has an inbuilt water cooling system that can work if attached with an external motor. With multiple trial and error experiments with the orientation of the module, coring from the back side gives cleaner samples when compared to the front side. This is mainly because the glass does not get stuck inside the coring bit as compared to the rear side. To simplify the approach, the junction box along with the laminate piece can be cut and sent to the TCLP labs as such for their crushing and testing. Since the junction box and the laminate above the junction box typically contain the large amount of interconnect ribbons, this piece can be considered the worst-case scenario. If the worst-case scenario is determined to be complying with the requirement of the standard, then it can be concluded that there is no further testing needed for the individual components of the module. It is cautioned that the test results obtained by this approach cannot be used for the pass/fail determination if the piece contains any toxic element exceeding the required limit.

The module that was tested did not exceed the EPA limit for any of the elements for the TCLP test. However, this cannot be used to make any decisive conclusions for the entire PV industry. More modules from different manufacturers need to be tested to obtain any objective evidence to make necessary conclusions.

5.2 TCLP testing procedure

The TCLP procedure has a few minimum requirements like, the particle size reduction. Per EPA Method 1311, “particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its 2 narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve. Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials." More data is needed in the image processing algorithm to determine the particle size in a broken module. Since the module was broken because of coring and it does not represent a field breakage. To get more accurate results, the module must be broken in a way similar to field breakage.

To make the process repeatable and reproducible, it is recommended to core four sets of identical samples and send two TCLP labs, two sets each. This is to identify any discrepancies in the coring procedure and to ensure that all the TCLP labs produce identical end results.

5.3 Image processing algorithm

The image processing was done with normal image as well as in UV fluorescence. The images in UV were more brighter and the cracks were more clearly distinguishable from the background. Since the cracks had to be traced manually to get more accurate results, four 2" x 2" areas are chosen at random and used for the image processing. By using artificial neural networks (ANN) bigger areas can be covered and more accurate results can be obtained.

5.4 Future Scope

The primary objective of the present work is to develop a sampling procedure to appropriately extract the samples from various parts of the module. The extracted samples are then sent to TCLP labs for testing and the test results are obtained. In this work, based on the test results obtained from the TCLP labs, we also demonstrate how to calculate the end results to determine the pass/fail requirements of the standard. In future, the results from additional modules can be obtained and stored in the form of a database. This database will be helpful in generating more reliable data to form the framework of a PV specific recycling regulation in the United States. Electronics product takeback legislation has been proposed in several European countries and the issue is discussed in several Asian countries (e.g., Japan, South Korea, Taiwan and Singapore). Environmental disposal and waste handling regulations, logistics and economics of product recycling and waste disposal affect the reasoning and practicality of recycling. With the right policies and enabling frameworks in place, the spawning of new industries that recycle and repurpose old solar PV panels will drive considerable economic value creation. This will be an essential element in the world's transition to a sustainable energy future.

References

[1] S. Weckend, A. Wade, and G. Heath, End-of-life management: Solar photovoltaic panels. 2016.

[2] C. Eberspacher, C. F. Gay, and P. D. Moskowitz, “Strategies for recycling CdTe photovoltaic modules,” Conf. Rec. IEEE Photovolt. Spec. Conf., vol. 1, no. Piscataway, NJ, United States, pp. 962–965, 1994.

[3] C. Eberspacher and V. M. Fthenakis, “Disposal and recycling of end-of-life PV modules,” Conf. Rec. Twenty Sixth IEEE Photovolt. Spec. Conf. - 1997, pp. 1067–1072, 1997.

[4] B. Bo and K. Yamamoto, “Characteristics of E-waste Recycling Systems in Japan and China,” World Acad. Sci. Eng. Technol. Int. J. Environ. Chem. Ecol. Geol. Geophys. Eng., vol. 4, no. 2, pp. 89–95, 2010.

[5] C. Honsberg and and S. Bowden, “PV CDROM.” [Online]. Available: http://pveducation.org/pvcdrom/modules/module-materials.

[6] D. de Rooij and N. D. Weimar, Comprehensive Guide to Solar PV Module Certifications. Sino Voltaics, 2016.

[7] First Solar, “First Solar CdTe Photovoltaic Technology : Environmental , Health and Safety Assessment,” pp. 1–50, 2013.

[8] PV Cycle Association, “Annual Report PV CYCLE 2015,” 2015.

[9] “PV Cycle R&D Projects.” [Online]. Available: http://www.pvcycle.org/organisation/our-rd-projects/.

[10] “EPA Method 1311 - Toxicity Characteristic Leaching Procedure” no. July 1992, pp. 1–35.