MULTI-CRITERIA ASSESSMENT OF ALTERNATIVE LEACHING PROCEDURES – A CASE OF SPENT LI-ION BATTERY WASTE

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by

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Submitted

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Dedicated to

Babaji,

the ultimate Lord

आनंद रूपां चितिशक्ति दीप्तां विद्यां परां ब्रह्मरसानुभूतिम्,
कारुण्यपूर्णाम् गुरुमूर्तिरूपाम् देवीं नमामः जगदीश्वरीम् त्वाम ।
माम् रक्ष नित्यं जगदावलंबे त्वमेव सत्यं जगज्जीवनींमता,
संसार जन्म ज्वररोग वैद्या माद्यां भजे हैड़ाखंड वासिनीम् ।।

CERTIFICATE

This is to certify that the thesis entitled "**Multi-Criteria Assessment of Alternative Leaching Procedures – A Case of Spent Li-Ion Battery Waste**", being submitted by **Ms. Aparna Sharma**, to the **Indian Institute of Technology Delhi** for the award of the degree of '**Doctor of Philosophy**' in Department of Civil Engineering is a record of the bonafide research work carried out by her under my supervision and guidance. She has fulfilled the requirements for the submission of this thesis, which to the best of my knowledge has reached the requisite standard.

The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any other degree or diploma.

Prof. Arvind K. Nema

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ABSTRACT

For the last few decades, the rapid growth of electronic industry has led to an increase in the spent li-ion or lithium-ion battery (LIB) waste, which subsequently has been posing a threat to the entire ecosystem as the waste disposal and management practices are still poor and outdated. All of this waste should be disposed of in a way specifically designed or permitted for them. But, as of today, due to the rising quantities, most of the wastes does not get segregated and end up as composite waste in landfills/dumpyards.

Ineffective hazardous waste management affect local communities practically in all countries. The wastes when come into contact with natural water produce toxic liquids (leachates) which are harmful for soil as well as the surrounding environment. The improper disposal of waste batteries can result in toxic metal contamination and pollute ground and surface water, soil, air, flora, fauna and also affect humans. The numerous negative effects of the waste dumping and the ever growing environmental awareness worldwide has created an urgent need to assess the toxicity/environmental impact of disposal/dumping of these wastes, which has further led to the development of numerous leaching procedures.

The current study has summarized the studies using globally available leaching tests. The past literature has been assessed thoroughly, describing the various types of leaching tests, the parameters and factors affecting the test results and the general scope and limitations. Delphi method has been applied to select some of the conventional leaching tests, which are the TCLP test, SPLP test, ASTM D 3987 test, EN 12457 test, GB 5086.1-1997 test and JLT-13 test. These tests were evaluated on the basis of chosen criteria; namely, leaching performance, cost, time duration, the ease of conducting experiments, and applicability/appropriateness to various use-case

scenarios. After generating an order of preference and finalizing the relative importance for each of the criterion (using AHP and Entropy method), tests were compared using an appropriate MCDA method (AHP and PROMETHEE-II) for determining the ranking. Out of the conventionally available tests, ASTM D 3987 was determined to be the most preferred one.

Now, considering the research gaps found on the basis of literature study, one of the most important one that seems to grab attention is the time which these tests require for leaching and evaluation. In order to reduce experimental cost, maximize leaching efficiency, decrease time duration of leaching procedure and increasing the ease of experimentation (by reducing labour time), alternate leaching procedures were proposed. These procedures were based on the sonication technique, which has been previously studied as an extraction process but not researched to its potential.

Numerous combinations of the sonication-based procedures (under two sets) for leaching metals out of spent li-ion battery waste were conducted. The first set consisted of procedures using different extraction fluids (extraction fluids for TCLP, SPLP & NEN and deionized water) for different time durations (10-60 min; 6 durations with 10 min time interval). For the second set, a novel hybrid leaching approach (sonication for 10-90 min, 9 durations with 10 min time interval along with end-to-end agitation times of 1,2 and 3 hours) was applied. The metal leaching efficiencies of all the procedures were calculated using TCLP leaching results as benchmark. Upon calculating leaching efficiencies for every metal, a leaching coefficient that represents leaching performance of relevant metals (Li, Co, Ni and Mn for the current study) was calculated for all the procedures. Based on leaching coefficient values, best time durations for maximum leaching (i.e., highest leaching coefficient) was selected.

The methods with best time durations for maximum leaching from all the types of alternate procedures (within sonication with different extraction fluids and the hybrid approach of sonication and end-to-end agitation) were compared with the conventional TCLP as well as ASTM D 3987 (most preferred according to the previous results in this study). The comparison was conducted on the basis of the four of the criteria shortlisted by Delphi (leaching performance, cost, time duration, and the ease of conducting experiments), and a preferential order was established for each one. Now the relative weights of all the criteria were determined using AHP, fuzzy AHP and Critic method. After finding out the orders of preference and the relative weights, the alternate procedures, as well as TCLP and ASTM D 3987 tests, were compared using another appropriate MCDA method (TOPSIS) for determining the ranking.

The final results indicated that sonication for 50 minutes using TCLP extraction fluid is the most preferred alternative among all the adopted hybrid as well as conventional approaches. Although this procedure has a relatively low leaching coefficient compared to conventional TCLP, its top ranking is due to its better performance in terms of experimental cost and time duration.

Keywords: Lithium-ion battery (LIB) waste, leachate, metal contamination, conventional leaching test, assessment criteria, sonication, MCDA methods, ranking.

सारांश

पिछले कुछ दशकों से, इलेक्ट्रॉनिक उद्योग के तेजी से विकास के कारण लिथियम-आयन बैटरी (एलआईबी) कचरे में वृद्धि हुई है, जो बाद में अपशिष्ट निपटान और प्रबंधन के रूप में पूरे पारिस्थितिकी तंत्र के लिए खतरा पैदा कर रहा है। प्रथाएं अभी भी खराब और पुरानी हैं। इस सभी कचरे का निपटान विशेष रूप से उनके लिए अनुमत तरीके से किया जाना चाहिए। लेकिन, आज की स्थिति में, बढ़ती मात्रा के कारण, अधिकांश कचरे को अलग नहीं किया जाता है और लैंडफिल/डंपयार्ड में मिश्रित कचरे के रूप में फेंक दिया जाता है।

अप्रभावी खतरनाक अपशिष्ट प्रबंधन व्यावहारिक रूप से सभी देशों में स्थानीय समुदायों को प्रभावित करता है। अपशिष्ट जब प्राकृतिक जल के संपर्क में आते हैं तो जहरीले तरल पदार्थ (लीचेट) उत्पन्न करते हैं जो मिट्टी के साथ-साथ आसपास के वातावरण के लिए हानिकारक होते हैं। अपशिष्ट बैटरियों के अनुचित निपटान के परिणामस्वरूप जहरीली धातु का संदूषण हो सकता है और जमीन और सतह के पानी, मिट्टी, वायु, वनस्पतियों, जीवों को प्रदूषित कर सकता है और मनुष्यों को भी प्रभावित कर सकता है। कचरे के डंपिंग के कई नकारात्मक प्रभावों और दुनिया भर में बढ़ती पर्यावरण जागरूकता ने इन कचरे के निपटान/डंपिंग के विषाक्तता/पर्यावरणीय प्रभाव का आकलन करने की तत्काल आवश्यकता पैदा की है, जिसके कारण कई लीचिंग प्रक्रियाओं का विकास हुआ है।

वर्तमान अध्ययन ने विश्व स्तर पर उपलब्ध लीचिंग परीक्षणों पर आधारित अध्ययनों को संक्षेप में प्रस्तुत किया है। पिछले साहित्य का पूरी तरह से मूल्यांकन, विभिन्न प्रकार के लीचिंग परीक्षणों, परीक्षण परिणामों को प्रभावित करने वाले मापदंडों और कारकों और सामान्य दायरे और सीमाओं का वर्णन करते हुए किया गया है। डेल्फी विधि का उपयोग करते हुए, कुछ पारंपरिक लीचिंग परीक्षणों का चयन किया गया है, जो TCLP परीक्षण, SPLP परीक्षण, ASTM D 3987 परीक्षण, EN 12457 परीक्षण, GB 5086.1-1997 परीक्षण और

JLT-13 परीक्षण हैं। इन परीक्षणों का मूल्यांकन चुने हुए मानदंडों के आधार पर किया गया है; जैसे, लीचिंग प्रदर्शन, लागत, समय अवधि, प्रयोग करने में आसानी, और विभिन्न उपयोग-केस परिदृश्यों के लिए उपयुक्तता। वरीयता क्रम तैयार करने और एएचपी और एंट्रॉपी विधि का उपयोग करके प्रत्येक कसौटी के सापेक्ष महत्व को अंतिम रूप देने के बाद, रैंकिंग निर्धारित करने के लिए उपयुक्त एमसीडीए विधि (एएचपी और प्रोमेथी-द्वितीय) का उपयोग करके परीक्षणों की तुलना की गई। पारंपरिक रूप से उपलब्ध परीक्षणों में से, एएसटीएम डी 3987 को सबसे उपयुक्त परीक्षण के रूप में निर्धारित किया गया है।

अब, साहित्य अध्ययन के आधार पर पाए गए शोध अंतरालों पर विचार करते हुए, सबसे महत्वपूर्ण में से एक जो ध्यान आकर्षित करता प्रतीत होता है वह है समय, जो इन परीक्षणों को लीचिंग और मूल्यांकन के लिए आवश्यक है। प्रायोगिक लागत को कम करने के लिए, लीचिंग दक्षता को अधिकतम करने, लीचिंग प्रक्रिया की समय अवधि को कम करने और प्रयोग की आसानी को बढ़ाने के लिए (श्रम समय को कम करके), वैकल्पिक लीचिंग प्रक्रियाओं का प्रस्ताव किया गया था। ये प्रक्रियाएँ सोनिकेशन तकनीक पर आधारित थीं, जिसका पहले एक निष्कर्षण प्रक्रिया के रूप में अध्ययन किया गया था, लेकिन इसकी क्षमता पर शोध नहीं किया गया था।

खर्च किए गए ली-आयन बैटरी कचरे से धातुओं की लीचिंग के लिए सोनिकेशन-आधारित प्रक्रियाओं (दो सेट के तहत) के कई संयोजन आयोजित किए गए थे। पहले सेट में अलग-अलग समय अवधि (10-60 मिनट; 10 मिनट के समय अंतराल के साथ 6 अवधि) के लिए अलग-अलग निष्कर्षण तरल पदार्थ (टीसीएलपी, एसपीएलपी और एनईएन और विआयनीकृत पानी के लिए निष्कर्षण तरल पदार्थ) का उपयोग करने वाली प्रक्रियाएं शामिल थीं। दूसरे सेट के लिए, एक नए हाइब्रिड लीचिंग दृष्टिकोण (10-90 मिनट के लिए सोनिकेशन, 10 मिनट के समय अंतराल के साथ 9 अवधि तथा 1, 2 और 3 घंटे का एंड-टू-एंड रोटेशन समय) लागू किया गया था। बेंचमार्क के रूप में टीसीएलपी लीचिंग परिणामों का उपयोग करके सभी प्रक्रियाओं की

धातु लीचिंग क्षमता की गणना की गई। प्रत्येक धातु के लिए लीचिंग क्षमता की गणना करने पर, एक लीचिंग गुणांक जो प्रासंगिक धातुओं (वर्तमान अध्ययन के लिए Li, Co, Ni और Mn) के संयुक्त लीचिंग प्रदर्शन को दिखाता है, की गणना सभी प्रक्रियाओं के लिए की गई थी। लीचिंग गुणांक मूल्यों के आधार पर, अधिकतम लीचिंग (यानी, उच्चतम लीचिंग गुणांक) के लिए सर्वोत्तम समय अवधि का चयन किया गया था।

सभी प्रकार की वैकल्पिक प्रक्रियाओं (विभिन्न निष्कर्षण तरल पदार्थों के साथ सोनिकेशन और सोनिकेशन और एंड-टू-एंड रोटेशन के हाइब्रिड दृष्टिकोण के भीतर) में से अधिकतम लीचिंग के लिए सर्वोत्तम समय अवधि वाले तरीकों की तुलना पारंपरिक टीसीएलपी के साथ-साथ एएसटीएम डी 3987 (इस अध्ययन में पिछले परिणामों के अनुसार सबसे उपयुक्त) से की गई। तुलना डेल्फी द्वारा चुने गए चार मानदंडों (लीचिंग प्रदर्शन, लागत, समय अवधि, और प्रयोग करने में आसानी) के आधार पर की गई और प्रत्येक के लिए एक अधिमान्य आदेश स्थापित किया गया था। अब एएचपी, फजी एएचपी और क्रिटिक पद्धति का उपयोग करके सभी मानदंडों के सापेक्ष वजन निर्धारित किए गए थे। वरीयता के क्रम और सापेक्ष भार का पता लगाने के बाद, वैकल्पिक प्रक्रियाओं के साथ-साथ TCLP और ASTM D 3987 परीक्षणों की रैंकिंग निर्धारित करने के लिए एक अन्य उपयुक्त MCDA विधि (TOPSIS) का उपयोग करके तुलना की गई।

अंतिम परिणामों ने संकेत दिया कि टीसीएलपी निष्कर्षण द्रव का उपयोग करके 50 मिनट के लिए सोनिकेशन सभी अपनाए गए हाइब्रिड के साथ-साथ पारंपरिक दृष्टिकोणों में सबसे उपयुक्त विकल्प है। हालांकि इस प्रक्रिया में पारंपरिक टीसीएलपी की तुलना में अपेक्षाकृत कम लीचिंग गुणांक है, फिर भी इसकी शीर्ष रैंकिंग प्रायोगिक लागत और समय अवधि के मामले में इसके बेहतर प्रदर्शन के कारण है।

कीवर्ड: लिथियम-आयन बैटरी (एलआईबी) अपशिष्ट, लीचेट, धातु संदूषण, पारंपरिक लीचिंग टेस्ट, मूल्यांकन मानदंड, सोनिकेशन, एमसीडीए के तरीके, रैंकिंग।

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List of Abbreviations, Acronyms and Symbols

CH_3COOH	Acetic Acid
Al	Aluminium
ANS	American National Standard
ASTM	American Standard Test Methods
CH_3COONH_4	Ammonium Acetate
NH_4OH	Ammonium Hydroxide
$(NH_4)_2SO_4$	Ammonium Sulphate
AHP	Analytic Hierarchy Process
ANP	Analytic Network Process
AHP-GM	Analytical Hierarchy Process Geometric Mean Method
AFNOR	Association Française de Normalisation
AAS	Atomic Absorption Spectrophotometer
ADD	Average daily dose
ABNT NBR	Brazilian National Standard
A-UCS	Appropriateness/Applicability to various use-case scenarios
Cd	Cadmium
Ca	Calcium
CSF	Carcinogenic Slope Factor
RI	Carcinogenic Risk
CEPA	China Environment Protection Agency
COPC	Contaminants of Potential Concern

CPCB	Central Pollution Control Board
Cr	Chromium
CAC	Coal-Ash Concrete
Co	Cobalt
Cu	Copper
DW	Deionized Water
DAF	Dilution-attenuation factor
DRET	Dredging Elutriate Test
ρ_b	Dry Bulk Density
EE	Ease of Experimentation
ELECTRE	ÉLimination Et Choix Traduisant la REalité (ELimination Et Choice Translating REality)
EF	Extraction Fluid
EoL	End-of-life
EPR	Extended Producer Responsibility
EVs	Electric Vehicles
NFX-31	French Waste Leaching Test
g-C3N4	Graphitic Carbon Nitride
HQ	Hazard Quotient
HCl	Hydrochloric Acid
HF	Hydrogen Fluoride
H_2O_2	Hydrogen Peroxide
NH_2OH	Hydroxylamine

$NH_2OH.HCl$	Hydroxyl Ammonium Chloride
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometer
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
IT	Information Technology
Fe	Iron
LE	Leaching Efficiency
Pb	Lead
LEAF	Leaching Environmental Assessment Framework
LIB/LIBs	Li-Ion Battery/Batteries
L/S ratio	Liquid to solid ratio
L/SA ratio	Liquid-to-surface area ratio
Li	Lithium
Mg	Magnesium
Mn	Manganese
MSW	Municipal Solid Waste
Hg	Mercury
MWLP	Mine Water Leaching Procedure
MCDA	Multi Criteria Decision Analysis
MEP	Multiple Extraction Procedure
MoEFCC	Ministry of Environment, Forest, and Climate Change
NTLT	Netherlands Tank Leaching Test
Ni	Nickel
HNO_3	Nitric Acid

NAIADE	Novel Approach to Imprecise Assessment and Decision Environments
RfD	Non-carcinogenic reference dose
PCLT	Pancake Column Leaching Test
$HClO_4$	Perchloric Acid
PBET	Physiologically Based Extraction Test
K	Potassium
PROMETHEE	Preference Ranking Organization METHod for Enrichment Evaluation
RAND Corp.	Research ANd Development
SBLP	Serial Batch Leaching Procedure
Ag	Silver
SBLT	Simple Batch Leaching Test
SBET	Simplified Bioaccessibility Extraction Test
Na	Sodium
Na_2CO_3	Sodium Carbonate
NaCN	Sodium Cyanide
NaOH	Sodium Hydroxide
K_d	Soil/soil-water partition coefficient
SET	Standard Elutriate Test
TVA	Swiss Leach Test
SGLP	Synthetic Groundwater Leaching Procedure
SPLP	Synthetic Precipitation Leaching Procedure
TOPSIS	Technique for Order Performance by Similarity to Ideal Solution
TCLP	Toxicity Characteristic Leaching Procedure

UHMI	Ultra-High Matrix Introduction
US EPA	United States Environment Protection Agency
USGS FLT	United States Geological Survey Field Leach Test
CEN/TS	Upflow Percolation Test
WET	Waste Extraction Test
WILT	Waste Interface Leaching Test
θ_w	Water-filled porosity
ZIF-67	Zeolitic Imidazolate Framework-67
Zn	Zinc