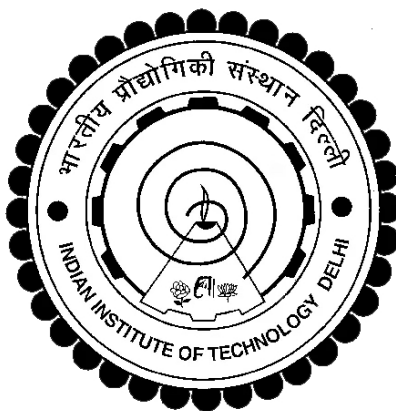


REMOVAL OF COLLOIDAL ASPHALTENE FROM SURFACES AND EFFECT OF AEROSOLS ON SOLAR POWER

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DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

MAY 2023

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by

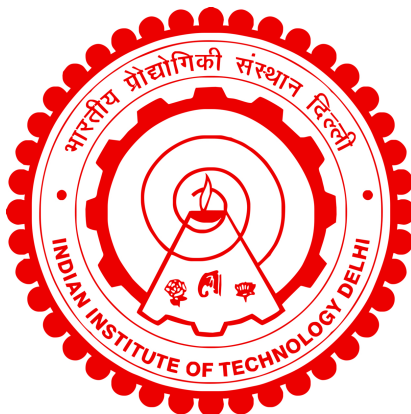
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Submitted

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

to the



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सब्र और हौसले की मिसाल देखना हो तो, सुन्ना मेरी अम्मा की कहानी।
टूटी हुई टांगो से करती थी काम ये कह कर, अभी मेरे बच्चे छोटे हैं।

*Dedicated to the Loving Memory of Amma Ji
who discovered the scientist in me long before I knew
what science is!*

Certificate

This is to certify that the thesis entitled “**Removal of Colloidal Asphaltene from Surfaces and Effect of Aerosols on Solar Power**”, submitted by **Syed Haider Abbas Rizvi** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Chemical Engineering, is a record of the original, bona fide research work carried out by him under our supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma to the best of our knowledge.

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Abstract

The study deals with problems in the energy sector resulting from sub-micron-sized particles suspended in fluid and their deposition on surfaces. In its first part, the study investigates the deposition and removal of colloidal asphaltene particles on contact surfaces in the crude oil industry. The second part of the study targets the solar energy sector, where aerosols in the atmosphere and particulate matter deposition on solar panels cause a reduction in light intensity.

With an increased demand for oil on a global scale, heavy oil (low API) that contains a considerable amount of asphaltene has captured the interest of oil producers. Asphaltene deposition on the surfaces in contact is a severe problem for the crude oil industry. The prospect of the first half of the study is to remove asphaltene by shear forces with pH-controlled conditions and ionic surfactants in aqueous media. The deposition occurs on glass surfaces from an asphaltene dispersion in heptane, mimicking the possible reservoir conditions. The removal is carried out in a parallel plate channel where controlling the shear rates tune the hydrodynamic forces on the surface. The flow inside the apparatus is of the order of Reynolds number from 10^3 to 10^4 . The study hypothesizes that detachment will occur when the hydrodynamic forces overcome the adhesion forces binding the asphaltene with asphaltene or asphaltene with the glass surface. The electrostatic double-layer charges in the medium affect the removal efficiency. The study correlates the zeta potentials for asphaltene under pH-conditioned aqueous media with the removal efficiency. Atomic force microscopy characterizes the extent of deposition and asphaltene removal in terms of surface roughness and fractional volume on the surface.

The results show that the aqueous media pH significantly affects asphaltene's roughness and fractional volume. At extreme pH values (2-3 or 8-10), the hydrophilicity of asphaltene increases due to the ionization of functional groups, causing more significant swelling of the asphaltene aggregates. The removal efficiency increases proportionally with the hydrodynamic forces and the pH. The anionic surfactants adsorb on asphaltene surfaces with hydrophobic interactions that stabilize surface asphaltene, resulting in inefficient removal. The cationic surfactants adsorb on negatively charged asphaltene surfaces through acid-base or electrostatic interactions, significantly increasing removal efficiency. The study provides strategies to remove

surface-deposited asphaltene based on their effective zeta potential with asphaltenes in crude oil.

The work's second part studied the solar beam's attenuation due to particulate matter suspended in the atmosphere and deposited on the PV modules. The radiative transfer model, *Py6S* approximates the total irradiance reaching the earth's surface, assuming absorption by gases and extinction due to aerosols. The model's accuracy is compared with ground measurements by pyranometers considering no or partial cloud cover. The deviations are more prominent during the monsoon and post-monsoon periods than pre-monsoon. The study also compares the losses due to soiling between two pyranometers, of which one is regularly cleaned. The study constitutes eight cycles of 21 days each, constituting months from March to November, and estimates soiling losses as a function of particulate matter deposition per unit area. The findings report that soiling losses vary across months, where meteorological parameters such as rainfall and relative humidity play a crucial role.

Moreover, soiling loss strongly correlates to the regional ambient particulate matter concentrations, size distribution, and chemical composition. Estimating irradiance as a function of air quality is required to evaluate power production by a solar plant. Soiling loss estimations are necessary to plan for a plant's cleaning cycles and accurate solar power generation predictions.

सारांश

यह अध्ययन तरल पदार्थ में निलंबित कण पदार्थ और सतहों पर निलंबित कण पदार्थ के जमाव के परिणामस्वरूप ऊर्जा क्षेत्र में समस्याओं से संबंधित है। अपने पहले भाग में, अध्ययन कच्चे तेल उद्योग में संपर्क सतहों पर कोलाइडल एस्फाल्टीन कणों के जमाव और हटाने की सम्भवता को दर्शित करता है। अध्ययन का दूसरा भाग सौर ऊर्जा क्षेत्र को लक्षित करता है, जहां वायुमंडल में एरोसोल और सौर पैनलों पर कणों का जमाव प्रकाश में कमी का कारण बनता है।

वैश्विक स्तर पर तेल की बढ़ती मांग को देखते हुवे, भारी तेल जिसमें काफी मात्रा में एस्फाल्टीन होता है, तेल उत्पादकों का अपनी ओर आकर्षित कर लिया है। संपर्क में सतहों पर एस्फाल्टीन का जमाव कच्चे तेल उद्योग के लिए एक गंभीर समस्या है। इस अध्ययन का पहले भाग, जलीय मीडिया में पीएच-नियंत्रित स्थितियों और आयनिक सर्फैक्टेंट के साथ कतरनी बलों द्वारा एस्फाल्टीन को संपर्क सतहों से हटाने पर केंद्रित है। कांच की स्लाइड को हेप्टेन और एस्फाल्टीन के डिस्पersion द्वारा निक्षेप किया गया है, जो संभावित तेल जलाशय की स्थिति की नकल करता है। निष्कासन एक समानांतर प्लेट चैनल में किया जाता है जहां कतरनी बल को नियंत्रित करने से सतह पर हाइड्रोडायनामिक बलों को समायोजित किया जाता है। तंत्र के अंदर प्रवाह 10^3 से 10^4 तक रेनॉल्ड्स संख्या के क्रम का है। अध्ययन का अनुमान है कि अलगाव तब होगा जब हाइड्रोडायनामिक बल कांच की सतह के साथ एस्फाल्टीन या एस्फाल्टीन के साथ एस्फाल्टीन को बांधने वाले आसंजन बलों से श्रेष्ठ हो जाएं। माध्यम में इलेक्ट्रोस्टैटिक डबल-लेयर चार्ज एस्फाल्टीन के हटाने की दक्षता को प्रभावित करते हैं। अध्ययन में यह सम्बंधित किया गया है की पीएच वातानुकूलित जलीय मीडिया में जीटा क्षमता के फेर बदल से एस्फाल्टीन हटाने की दक्षता प्रभावित होती है। एटॉमिक फ़ोर्स माइक्रोस्कोपी द्वारा सतह का खुरदरापन और सतह पर आंशिक एस्फाल्टीन की मात्रा परिभाषित किया गया है।

परिणाम बताते हैं कि जलीय मीडिया पीएच, एस्फाल्टीन सतह के खुरदरेपन और आंशिक मात्रा को महत्वपूर्ण रूप से प्रभावित करता है। चरम पीएच मान (२-३ या ८-१०) पर, कार्यात्मक समूहों के आयनीकरण के कारण एस्फाल्टीन की हाइड्रोफिलिसिटी बढ़ जाती है, जिससे एस्फाल्टीन समुच्चय की उभाड़ हो जाती है। हटाने की दक्षता, हाइड्रोडायनामिक बलों और पीएच के साथ आनुपातिक रूप से बढ़ जाती है। आयनिक सर्फैक्टेंट हाइड्रोफोबिक इंटरैक्शन के साथ एस्फाल्टीन सतहों पर सोखते हैं जो सतह एस्फाल्टीन को स्थिर करते हैं, जिसके परिणामस्वरूप अक्षम निष्कासन होता है। धनायनित सर्फैक्टेंट एसिड-बेस या इलेक्ट्रोस्टैटिक इंटरैक्शन के माध्यम से नकारात्मक रूप से चार्ज किए गए एस्फाल्टीन सतहों पर सोखते हैं, एवं हटाने की दक्षता में काफी वृद्धि करते हैं। अध्ययन कच्चे तेल में एस्फाल्टीन के साथ उनकी प्रभावी जीटा क्षमता के आधार पर सतह पर जमा एस्फाल्टीन को हटाने के लिए रणनीति प्रदान करता है।

कार्य के दूसरे भाग ने वातावरण में निलंबित कणों और पीवी मॉड्यूल पर जमा होने के कारण सौर बीम के क्षीणन का अध्ययन किया गया है। रेडिएटिव ट्रांसफर मॉडल, पृथ्वी की सतह तक पहुंचने वाले कुल विकिरण, गैसों द्वारा अवशोषण और एरोसोल के कारण विलुप्त होने का अनुमान लगाता है। मॉडल की सटीकता की तुलना बिना या

आंशिक क्लाउड कवर पर विचार करते हुए पाइरनोमीटर द्वारा जमीनी माप के साथ की जाती है। पूर्व-मानसून की तुलना में मानसून और मानसून के बाद की अवधि के दौरान विचलन अधिक प्रमुख हैं। अध्ययन में दो पायरेनोमीटरों के बीच में धुल के जमा होने से होने वाले नुकसान की भी तुलना की गई है। इनमें से एक प्यारनोमीटर को नियमित रूप से साफ़ किया जाता है, अथवा दूसरे पर धुल जमा होने दिया जाता है। अध्ययन में प्रत्येक 21 दिनों के आठ चक्र शामिल हैं, जो मार्च से नवंबर तक के महीनों का गठन करते हैं, और प्रति इकाई क्षेत्र में कणों के जमाव के एक समारोह के रूप में धुल के नुकसान का अनुमान लगाते हैं। निष्कर्ष बताते हैं कि धुल के जमाव से होने वाले नुकसान प्रत्येक महीनों में भिन्न होते हैं, जहां वर्षा और सापेक्ष आर्द्रता जैसे मौसम संबंधी पैरामीटर महत्वपूर्ण भूमिका निभाते हैं।

इसके अतिरिक्त, सौर पैनल पे जमाव की हानि परिवेशी कणों की सांद्रता से दृढ़ता से संबंधित है। सौर संयंत्र द्वारा बिजली उत्पादन का अनुमान लगाने के लिए वायु गुणवत्ता के कार्य के रूप में विकिरण का अनुमान लगाना आवश्यक है। एक संयंत्र के सफाई चक्र और सौर ऊर्जा उत्पादन की सटीक भविष्यवाणियों की योजना बनाने के लिए धुल के जमाव के नुकसान का आकलन आवश्यक है।

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Abbreviations

AERONET	A erosol R obotic N etwork
AOP	A sphaltene O nset P ressure
AFM	A tomic F orce M icroscopy
AOD	A erosol O ptical D epth
AQI	A ir Q uality I ndex
ASTM	A merican S ociety for T esting and M aterials
BSRN	B aseline S urface R adiation N etwork
CMC	C ritical M icelle C oncentration
COT	C loud O ptical T hickness
CTAB	C etyl T rimethyl A mmonium B romide
DHI	D iffuse H orizontal I rradiance
DI	D e- I onized
DNI	D irect N ormal I rradiance
ECMWF	E uropean C entre M edium- R ange W eather F orecast
EOR	E nhanced O il R ecovery
GAN	G andhinagar
GHI	G lobal H orizontal I rradiance
GUR	G urgaon
HOW	H owrah
HPLC	H igh P erformance L iquid C Chromatography
IEP	I so- E lectric P oint
IMD	I ndian M eteorological D epartment
IODC	I ndian O cean D ata C overage
ISRO	I ndian S pace R esearch O rganization
MERRA	M odern E ra R etrospective analysis for R esearch and A pplications
MPE	M ean P ercentage E rror

NASA	N ational A eronautics S pace A dministration
PBLH	P lanetary B oundary L ayer H eight
PM	P articulate M atter
PV	P hoto- V oltaics
RH	R elative H umidity
RMSE	R oot M ean S quared E rror
RPM	R evolutions P er M inute
RTM	R adiative T ransfer M odel
SDS	S odium D odecyl S ulfonate
6S	S econd S imulation of the S atellite S ignal in the S olar S pectrum
TIR	T iruvallur
TOA	T op O f A tmosphere
TMY	T ypical M eteorological Y ear

Physical Constants

Density of Water	ρ	$=$	1.0×10^3	kg.m^{-3}
Hamaker Constant for Asphaltene	$A_{asphaltene}$	$=$	6.0×10^{-20}	J
Hamaker Constant for Silica	A_{silica}	$=$	6.5×10^{-20}	J
Hamaker Constant for Water	A_{water}	$=$	3.70×10^{-20}	J
Viscosity of Water	μ	$=$	8.9×10^{-4}	N.s.m^{-2}
Solar Constant	I_{SC}	$=$	1380	W.m^{-2}

Nomenclature

$\dot{\gamma}$	Shear Rate,	s^{-1}
a_c	Effective Contact Radius,	nm
d	Diameter,	nm
h	Separation Between Plates,	m
F_{adh}	Adhesion Force,	N
F_D	Sliding Force,	N
F_L	Lift Force,	N
I_{obs}	Instrument Observed Irradiance,	$W.m^{-2}$
I_{sim}	Model Simulated Irradiance,	$W.m^{-2}$
$I_{surface}$	Surface Irradiance,	$W.m^{-2}$
I_{TOA}	Top Of Atmosphere Irradiance,	$W.m^{-2}$
K_c	Clearness Index,	dimensionless
M_D	Moment of Rotational Component,	N.m
M_h	Total Hydrodynamic Torque,	N.m
$PM_{2.5}$	Particulate Matter size lesser than 2.5 μm ,	$\mu g.m^{-3}$
PM_{10}	Particulate Matter size lesser than 10 μm ,	$\mu g.m^{-3}$
PYR_c	Clean Pyranometer reading,	$W.m^{-2}$
PYR_s	Soiled Pyranometer reading,	$W.m^{-2}$
Re	Reynolds Number,	dimensionless
R_{max}	Maximum Height,	nm
R_q	Root-mean-square of Roughness,	nm
SL	Soiling Loss,	%
ΔSL	Change in Soiling Loss per day,	$\%.day^{-1}$
ΔSL_{dry}	Change in Soiling Loss per day evaluated during dry period,	$\%.day^{-1}$
U_{95}	95% Confidence Interval,	%
U_{BSRN}	Uncertainty In BSRN's Ground Irradiance,	%

v_{avg}	Average Velocity,	m.s^{-1}
V_i	Volume of Pixel,	nm^3
V_t	Volume of Aggregate,	nm^3
$\bar{V}_t$	Normalized Volume of Asphaltene,	dimensionless
Z_i	Height of Pixel,	nm