Major, Trace and Rare Earth Elements in Sediments of the Julian Adame-Alatorre Dam by Instrumental Neutron Activation Analysis

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Abstract

The rapid industrial development in Mexican regions during recent decades has a side effect by the introduction of toxic metals, fertilizers, or pesticides in many ecosystems. Sediment cores were collected from eight locations of Julian Adame-Alatorre dam located in Municipality of Villanueva in the State of Zacatecas, México, were analyzed for 32 major, trace, and rare earth elements (As, La, Lu, Nd, Sm, U, Yb, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, Zr, Al, Ba, Ca, Dy, K, Mn, Na, Ti, V), in order to estimate the health risk, by instrument neutron activation analysis (INAA); using thermal neutron fluxes of 8 x 10^{13} and 5 x 10^{13} n cm^{-2} s^{-1}, for short and long irradiations, respectively. The results of the contamination levels for elements such as As, Ba, Cr, Fe, Mn, Ta, V, and Zn were compared with the Mexican regulations and the guidelines of USEPA.

1. INTRODUCTION

The rapid industrial development in Mexican regions during recent decades has a side effect by the introduction of toxic metals, fertilizers, or pesticides in many ecosystems. As well, the demand of rare-earth elements (REEs) for industrial applications is increasing rapidly; and concurrently the environmental contamination by REEs. General public has great concerns about the environmental quality of a region to where they are living, to maintain their healthy life style [1, 2]. These pollutants released into the environment enter the atmosphere and hydrological circulations and are finally deposited on riverbeds, in reservoirs or river deltas. Sediment is known as a sink for trace elements like heavy metals produced from anthropogenic sources such as the discharge of municipal, residential and industrial waste materials, and thus must be one of

the environmental indicators. A lot of researches have been executed to identify a contamination level of toxic metals in the environmental sediment samples.

Each country has issued its own regulations stating the limits of concentrations of heavy metals or other pollutants that can be considered acceptable or dangerous. In México, these limits have been established by the Minister of the Environmental Protection and publish in the Mexican Official Norm NOM-147-SEMARNAT/SSA1-2004, and it refers to soil and sediments for agricultural, residential, commercial and industrial uses [1, 3]. They include both soil and sediments, but between these categories there are no differences. In this way, to be considered as a pollutant, any potentially harmful compound must satisfy simultaneously two criteria: (1) to present an increased concentration near the sediment surface and (2) to exceed the legal limits. In the present work, the comparison of the results was carried out with the limits of concentrations established by the Mexican Official Norm; and as well as the concentration guidelines of USEPA in this matter [4].

High precision nuclear technique of quantitative analysis such as instrumental neutron activation analysis (INAA) is currently used in the investigation of environmental samples such as sediments or soils due to the very high sensitivity. In the present work, this analytical technique was used to study the concentration of major, trace, and rare-earth elements (REEs) in eight sedimentary cores that were collected from the Julian Adame-Alatorre dam, located in the Municipality of Villanueva in the State of Zacatecas, México. This study aimed at applying INAA for the analysis of eight sediment cores to uncover the existence of any pollution in Julian Adame-Alatorre dam with the elements in question [2, 5].

2. EXPERIEMENTAL

2.1. Description of Field Area

The Unit of The Chique-Tayahua counts of two storage dams, The Chique with 140 x10^6 m^3 of capacity and Julian Adame-Alatorre with 38 x10^6 m^3 of capacity; they are sources of supply with waters of draining of the river of Juchipila; this unit is located to the Southeastern of the state of Zacatecas to an approximated distance of 130 km from its capital of the City of Zacatecas. The geographic location of Julian Alatorre dam is at Latitude 22° 07' 12" N and Longitude 102° 51' 49" W; and Altitude 1,722 amsl (Fig.1). The Julian Adame-Alatorre dam is considerably influenced by mining industry, and it is affected by traditional and intensive agriculture. The dam water is used to satisfy the needs of intensive agriculture. Also, there is an aquaculture center that produces Golden Tilapia (Oreochromis aureus) and Rocky Mountain Tilapia (O. niloticus X O. aureus).

2.2. Sampling and Sample Preparation

Sediment samples were collected from eight locations of Julian Adame-Alatorre dam located in Municipality of Villanueva in the State of Zacatecas, México, during the spring season of 2003. The location of Julian Adame-Alatorre dam site is indicated in Fig. 1; and two samples were collected in each quadrant, in order to get representative samples. Eight samples at the sampling

points were collected in accordance with the depths, which were taken from the upper 10 cm of the dam bottom by using a piston corer. The resulting cores with a diameter of 3.81 cm were stored in polyethylene bags [6, 7]. The sediment samples have been prepared into finely ground homogenous material and the powdered sediment samples were dried for 24 hours in an oven at 100 °C to remove any water present.

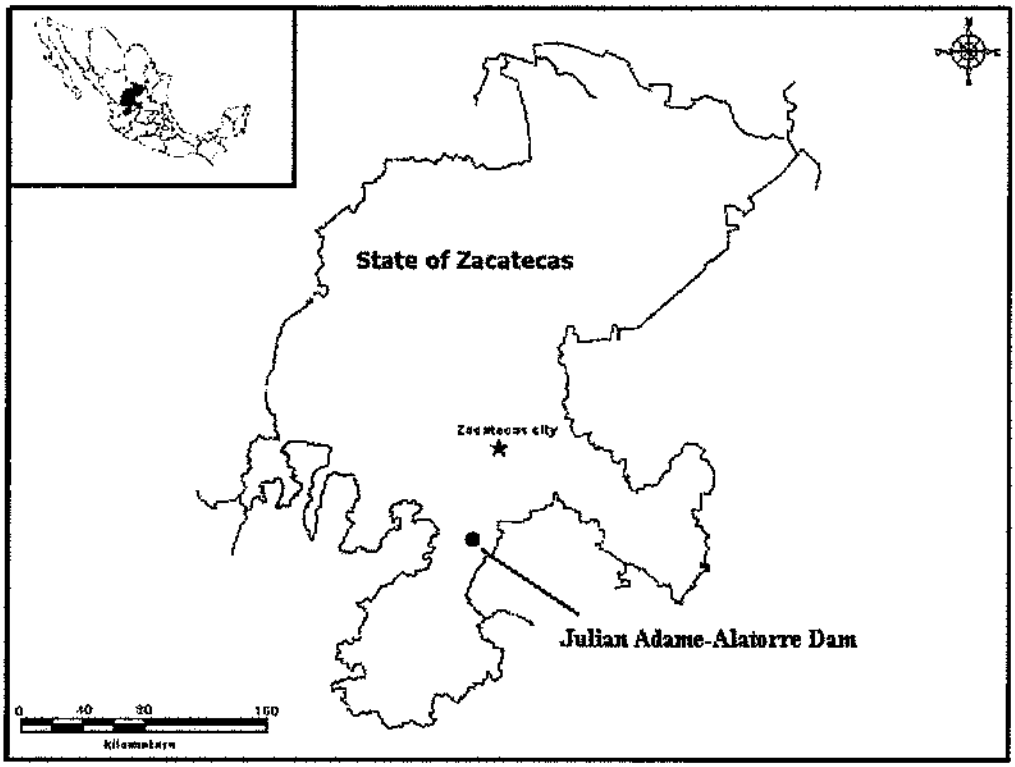

Figure 1. Map showing the location of Julian Adame-Alatorre dam site

2.3. Instrumental Neutron Activation Analysis

For an INAA, aliquots of powdered sediment samples weighing 150 mg were placed in separate polyethylene vials and high-purity quartz vials used for short and long irradiations, respectively, at Missouri University Research Reactor (MURR) of the University of Missouri-Columbia, USA. The irradiation and counting parameters utilized for the element analyses are reported in Table I. The short-irradiation samples in polyvials were sequentially irradiated in a neutron flux of 8.0 x 10^{13} n cm^{-2} s^{-1} for five seconds, allowed to decay for 25 min, and then counted for 12 min each on a high-purity intrinsic germanium (HP Ge) detector, 25% relative efficiency, FWHM resolution of 1.85 keV for the 1332 keV gamma ray of ^{60}Co [1,2, 6,8]. Qualitative and quantitative analysis can be achieved by analysis of gamma-lines in the gamma-spectrum detected and registered by HP Ge detector and its associated electronic circuit.

Table I. Irradiation and counting conditions

Elements and Half-Life	Irradiation flux ($n\ cm^{-2}\ s^{-1}$)	Irradiation time	Decay time	Counting time
Short-lived elements: Al, Ba, Ca, Dy, K, Mn, Na, Ti, V	$8x10^{13}$	5 s	25 min	12 min
Medium-lived elements: As, La, Lu, Nd, Sm, U, Yb	$5x10^{13}$	24 h	7 days	30 min
Long-lived elements: Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, Zr	$5x10^{13}$	24 h	21 days	2.5 h

2.4. INAA Measurements

In this work, the analytical technique employed was INAA using the MURR reactor for the activation and the HP Ge detector was connected to an ORTEC system for gamma –ray spectroscopy. Elements measured from the short-irradiation samples were the following: Al, Ba, Ca, Dy, K, Mn, Na, Ti, and V. The long-irradiation samples in quartz vials were irradiated as a single bundle by a neutron flux of 5.0 $x10^{13}$ n cm^{-2} s^{-1} for a period of 24 h. Two counts were made on the samples after long irradiation also using a HP Ge detector. The first count for 30 min per sample was made after the samples decayed for 7 days and enabled successful measurement of the following medium-lived elements: As, La, Lu, Nd, Sm, U, and Yb. The second count for 2.5 h per sample was made after the samples decayed for an additional 14 days and enabled measurement of the following long-lived elements: Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr. The REE concentrations in our samples were measured for the elements La, Sm, Ce, Nd, Eu, Yb and Lu. Concentrations in the unknown samples were determined relative to the NIST standards SRM-1633a Coal Flyash and SRM-278 Obsidian Rock which were prepared and irradiated under identical conditions with the sediment samples. Measurement uncertainties for almost of the elements are under 5 percent.

In this work, optimum conditions were used to obtain interference free photo-peaks of the desired elements. Irradiation, cooling and counting time were optimized depending on the half-lives of elements analyzed, in order to improve the ratio between the relative activity of each element and the bulk activity of the matrix. Also, the Table II shows the estimated detection limits for INAA using decay gamma rays. Assuming irradiation in a reactor neutron flux of $1x10^{13}$ n cm^{-2} s^{-1}, at University of Missouri Research Reactor (MURR), University of Missouri-Columbia, USA [8].

Table II. Estimated detection limits for INAA using decay gamma rays. Assuming irradiation in a reactor neutron flux of $1x10^{13}$ n cm^{-2} s^{-1}.

Sensitivity (picograms)	Elements
1	Dy, Eu
1 - 10	In, Lu, Mn
10 - 100	Au, Ho, Ir, Re, Sm, W
100 - 1E3	Ag, Ar, As, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, V, Yb
1E3 - 1E4	Al, Ba, Cd, Ce, Cr, Hg, Kr, Gd, Ge, Mo, Na, Nd, Ni, Os, Pd, Rb, Rh, Ru, Sr, Te, Zn, Zr
1E4 - 1E5	Bi, Ca, K, Mg, P, Pt, Si, Sn, Ti, Tl, Xe, Y
1E5 - 1E6	F, Fe, Nb, Ne
1E7	Pb, S

3. RESULTS AND DISCUSION

The analytical results of 32 elements from the eight sediment samples are presented in Tables III, IV, and V according to their respective radioisotope half-life, short, medium and large. The elements determined were As, La, Lu, Nd, Sm, U, Yb, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, Zr, Al, Ba, Ca, Dy, K, Mn, Na, Ti, and V. For the determination of several rare earth elements, INAA is also favorable, such as, Ce, Eu, La, Lu, Nd, Sm, and Yb. The mean concentrations of the major elements such as Al, Ca, Fe, K, Na, and Ti were 7.30%, 0.87%, 2.31%, 2.80%, 1.36% and 0.33%, respectively. Concentrations of the hazardous elements such as As, Ba, Cr, Mn, Sb, V and Zn were 4.6 mg kg^{-1}, 894.3 mg kg^{-1}, 18.6 mg kg^{-1}, 387.3 mg kg^{-1}, 0.72 mg kg^{-1},39.9 mg kg^{-1}, and 77.3 mg kg^{-1}, respectively. The relative errors (%) of most of the determined elements were within 5%.

Table III. Concentrations of major and trace elements in sediments of Julian Adame Alatorre dam for short-lived elements (in mg kg^{-1})

Element	JA01	JA02	JA03	JA04	JA05	JA06	JA07	JA08	Mean
Al (%)	7.16	7.67	7.71	7.69	6.85	6.65	6.76	7.88	7.30
Ba	669.8	980.2	920.6	840.5	1139.1	1112.2	607.4	884.9	894.3
Ca (%)	0.83	0.83	0.97	0.92	0.68	0.60	0.77	1.32	0.87
Dy	7.72	8.09	6.89	6.97	4.37	4.39	7.15	7.42	6.63
K (%)	2.43	3.00	2.66	2.77	3.39	3.24	2.66	2.28	2.80
Mn	290.3	751.5	333.6	403.6	347.8	327.7	397.0	247.3	387.3
Na (%)	1.17	1.15	1.31	1.24	1.90	1.87	1.22	1.00	1.36
Ti (%)	0.31	0.30	0.31	0.34	0.35	0.37	0.30	0.35	0.33
V	46.9	47.6	43.6	44.7	28.8	25.7	30.5	51.2	39.9

Table IV. Concentrations of major and trace elements in sediments of Julian Adame Alatorre dam for medium-lived elements (in mg kg^{-1})

Element	JA01	JA02	JA03	JA04	JA05	JA06	JA07	JA08	Mean
As	< 2.8	5.7	3.2	3.4	6.5	4.8	6.8	< 3.4	4.6
La	39.7	57.8	43.3	48.3	30.0	29.8	38.0	43.9	41.3
Lu	0.57	0.75	0.62	0.68	0.43	0.43	0.64	0.57	0.59
Nd	33.7	57.6	38.4	40.6	24.7	24.7	37.6	42.8	37.5
Sm	7.48	11.33	8.19	9.06	5.09	4.97	7.82	8.07	7.75
U	6.13	5.01	3.30	4.62	2.83	3.77	4.94	3.49	4.26
Yb	3.85	5.35	4.00	4.96	2.93	2.90	4.63	3.97	4.07

Table V. Concentrations of major and trace elements in sediments of Julian Adame Alatorre dam for large-lived elements (in mg kg^{-1})

Element	JA01	JA02	JA03	JA04	JA05	JA06	JA07	JA08	Mean
Ce	72.6	104.0	82.9	90.5	60.7	60.2	71.8	84.5	78.4
Co	3.22	7.60	6.00	5.39	2.51	2.60	4.09	5.87	4.66
Cr	14.8	25.7	31.4	24.0	6.6	7.8	15.5	22.8	18.6
Cs	12.5	30.8	26.1	23.7	4.9	4.7	12.2	18.9	16.7
Eu	1.14	1.70	1.28	1.41	1.15	1.15	1.13	1.16	1.27
Fe (%)	1.92	3.31	2.87	2.75	1.54	1.51	2.05	2.51	2.31
Hf	12.2	10.3	12.0	12.0	11.2	10.7	11.7	9.5	11.2
Rb	140.0	174.2	145.4	165.9	157.6	155.1	142.5	125.8	150.8
Sb	0.71	0.92	0.85	0.83	0.50	0.54	0.70	0.69	0.72
Sc	6.09	9.88	8.56	7.73	3.53	3.38	6.08	7.79	6.63
Sr	99.8	195.3	140.0	130.2	115.9	103.7	119.6	94.9	124.9
Ta	1.57	1.74	1.68	1.73	1.49	1.49	1.60	1.24	1.57
Tb	1.14	1.64	1.16	1.39	0.75	0.69	1.18	1.06	1.13
Th	13.1	15.7	13.5	13.6	11.4	11.0	12.5	12.4	12.9
Zn	70.8	93.4	131.9	78.0	43.3	48.6	73.4	79.1	77.3
Zr	308.0	265.3	305.7	318.3	325.0	272.4	284.4	239.3	289.8

INAA is also favorable for the determination of several rare earth elements (REE), such as, Ce, Eu, La, Lu, Nd, Sm, and Yb. The Table VI shows the mean concentration of the REEs in the eight sediment samples in ppm.

For the assessment of the contamination level of the Julian Adame-Alatorre dam, the elemental concentrations for As, Ba, Cr, Fe, Mn, and Zn were compared with the guidelines of USEPA [USEPA, 1993], which is presented in Table VII. By this comparison, it can be concluded that As in seven samples, Cr and Zn in two samples were moderately polluted; Ba in eight samples, Fe in four samples, and Mn in one sample were highly polluted in some sampling locations of the sediments of Julian Adame-Alatorre. On the other hand, element also generally known to be associated with air pollutants, such as, As, showed moderately polluted [9-10].On the other hand, for the assessment of the contamination level of the Julian Adame-Alatorre dam, the elemental

concentrations for As, Ba, Cr, Ta, and V were compared with the guidelines of México, NOM-147-SEMARNAT/SSA1-2004, which is presented in Table VIII. By this comparison, it can be concluded that all concentration values are bellow guidelines of México.

Table VI. Concentrations of rare-earth elements in sediments of Julian Adame-Alatorre dam (in mg kg^{-1})

Element	JA01	JA02	JA03	JA04	JA05	JA06	JA07	JA08	Mean
Ce	72.6	104.0	82.9	90.5	60.7	60.2	71.8	84.5	78.4
Eu	1.14	1.70	1.28	1.41	1.15	1.15	1.13	1.16	1.27
La	39.7	57.8	43.3	48.3	30.0	29.8	38.0	43.9	41.3
Lu	0.57	0.75	0.62	0.68	0.43	0.43	0.64	0.57	0.59
Nd	33.7	57.6	38.4	40.6	24.7	24.7	37.6	42.8	37.5
Sm	7.48	11.33	8.19	9.06	5.09	4.97	7.82	8.07	7.75
Yb	3.85	5.35	4.00	4.96	2.93	2.90	4.63	3.97	4.07

Table VII. Comparison of elemental contents with USEPA guidelines (mg kg^{-1})

Element	USEPA guidelines for classification of great lakes harbor sediments			Present work	
	Not polluted	Moderately polluted	Heavily polluted	Range	Mean
As	<3	3-8	>8	2.8-6.8	4.6
Ba	<20	20-60	>60	607.4-1139.1	894.3
Cr	<25	25-75	>75	6.6-31.4	18.6
Fe	<17,000	17,000-25,000	>25,000	15,100-33,100	23,100
Mn	<300	300-500	>500	247.3-751.5	387.3
Zn	<90	90-200	>200	43.3-131.9	77.3

Table VIII. Comparison of elemental contents with NOM-147-SEMARNAT/SSA1-2004 guidelines of México (mg kg^{-1})

Element	NOM-147-SEMARNAT/SSA1-2004 guidelines of México		Present work	
	Commercial, agricultural, and residential use	Industrial use	Range	Mean
As	22	260	2.8-6.8	4.6
Ba	5400	67000	607.4-1139.1	894.3
Cr*	280	510	6.6-31.4	18.6
Ta	5.2	67	1.24-1.74	1.57
V	78	1000	25.7-51.2	39.9

*Hexavalent Chromium

For a better overview of the data, the metal concentration variations in the sediments were plotted, see Figure 2. The As and Cr concentrations were multiplied by 10, and the Sb concentration was multiplied by 100 to improve the visualization of the data. For a better overview of the data, the rare-earth element concentration variations in the sediments were plotted, see Figure 3. The Eu and Lu concentrations were multiplied by 10, to improve the visualization of the data [11].

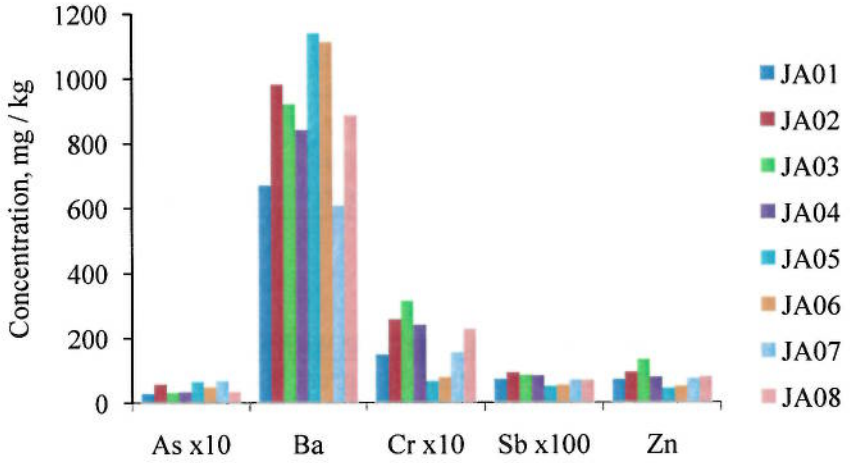

Figure 2. Concentrations of metal elements in sediments of Julian Adame-Alatorre dam

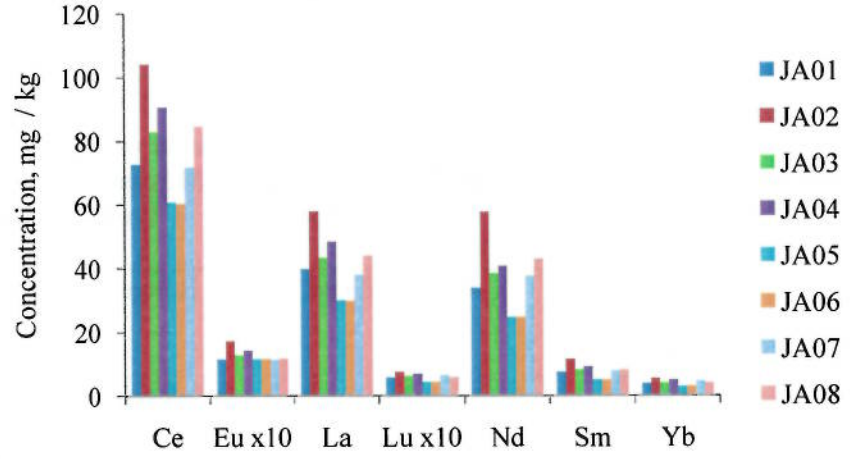

Figure 3. Concentrations of rare-earth elements in sediments of Julian Adame-Alatorre dam

Finally, the elements may be divided into the following three groups according to their median values [6]:

(1) Major elements (1 — 10%): Fe, Al, K, Na
(2) Minor elements (10 ppm — 1%): Ca, Ti, La, Nd, Ce, Cr, Cs, Hf, Rb, Sr, Th, Zn, Zr, Ba, Mn, V.
(3) Trace elements (<10 ppm): As, Lu, Sm, U, Yb, Co, Eu, Sb, Sc, Ta, Tb, Dy,

4. CONCLUSIONS

In this study, dam sediment samples were analyzed by INAA and 32 elements were determined. When the elemental contents for As, Ba, Cr, Fe, Mn, and Zn were compared with the guidelines of USEPA, dam sediments turned out to be moderately contaminated.

The difference in the elemental concentrations between guidelines of USEPA and guidelines of México is so high. The results of this study indicated that sediments from Julian Adame-Alatorre dam present concentration levels of As, Ba, Cr, Fe, Mn, and Zn higher than the not polluted USEPA guidelines values; and concentration levels of As, Ba, Cr, Ta, and V lower than residential use México Guideline values.

The main lesson learnt from the present study may be expressed as follows: (1) Sediments in the Julian Adame-Alatorre dam are contaminated with Ba, Fe, and Mn, in eight, three and one sediment samples, respectively; probably derived from air pollution, but the levels are low and indicate that atmospheric deposition in not a major contributing factor to the sediment contamination. (2) In all cases sediment concentrations of As, Ba, Cr, Ta, and V did not exceed the "minimum threshold of safety" according to Mexican legislation.

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DISCLAIMER

"Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Department of Energy".

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