



Subject: Calcium Sulfate for Environmental Remediation

From: Angela Hassell Date: 7 May 2013

Project: Water Quality Control Board – Reagent Evaluation

The Los Angeles Region of the California Regional Water Quality Control Board (WQCB) is in the process of evaluating chemistries for addition to the list of approved reagents for *in situ* remediation. The following sections describe the use of calcium sulfate for *in situ* metals stabilization for consideration of inclusion into the Los Angeles Region permit.

Source of Submission: ReSolution Partners, LLC

Identity of Reagent: Calcium sulfate (CaSO₄), CAS # 7778-18-9

Number of Field-scale

Applications to Date: ReSolution Partners is aware of one pilot-scale application

of this product as a source of sulfur for metals stabilization. It has had more widespread use as an alternate electron acceptor in the degradation of petroleum hydrocarbons. As the product is approved in other California jurisdictions, there may be additional sites where the product has been

applied.

Brief Rationale for

Inclusion in New WDR: See general chemistry information below.

General Chemistry Information

Calcium sulfate is a moderately water and acid soluble sulfate source for anaerobic stabilization of metals with the goal to form sulfide minerals. Under this remediation application, sulfate will convert to sulfide, which combines with metals to form insoluble mineral species. Calcium likely remains dissolved in solution unless site-specific conditions result in its precipitation or adsorption.

Attachment 1 provides an MSDS of the product. The product does not contain secondary chemicals that will release into the environment.





Project Examples

Calcium sulfate has been evaluated for *in situ* for metals stabilization at a site in New Jersey for stabilization of multiple heavy metals. A case study is presented in Attachment 2 for the bench-scale testing. In-field pilot tests have been completed and full-scale design is in progress.





Attachment 1

MSDS

Material Safety Data Sheet

Calcium sulfate, anhydrous, 99%

ACC# 97063

Section 1 - Chemical Product and Company Identification

MSDS Name: Calcium sulfate, anhydrous, 99% Catalog Numbers: AC217520000, AC217521000

Synonyms: Crysalba; Drierite; Thiolite

Company Identification:
Acros Organics N.V.
One Reagent Lane
Fair Lawn, NJ 07410

For information in North America, call: 800-ACROS-01 For emergencies in the US, call CHEMTREC: 800-424-9300

Section 2 - Composition, Information on Ingredients

CAS#	Chemical Name	Percent	EINECS/ELINCS
7778-18-9	Calcium sulfate, anhydrous	99	231-900-3

Hazard Symbols: XI Risk Phrases: 36/37

Section 3 - Hazards Identification

EMERGENCY OVERVIEW

Appearance: colorless to white powder. Hygroscopic (absorbs moisture from the air). **Caution!** Causes eye irritation. Causes respiratory tract irritation. May cause skin irritation.

Target Organs: None.

Potential Health Effects

Eye: Causes eye irritation. **Skin:** May cause skin irritation.

Ingestion: May cause digestive tract disturbances.

Inhalation: Causes respiratory tract irritation. Inhalation of dusts may cause nervous system complaints, ulceration of the mucous membranes of the nose and throat, epistaxis, headache, irritation and nervousness.

Chronic: No information found.

Section 4 - First Aid Measures

Eyes: Flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid immediately.

Skin: Get medical aid. Flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse.

Ingestion: If victim is conscious and alert, give 2-4 cupfuls of milk or water. Never give anything by mouth to an unconscious person. Get medical aid immediately.

Inhalation: Remove from exposure and move to fresh air immediately. If not breathing, give artificial respiration.

If breathing is difficult, give oxygen. Get medical aid.

Notes to Physician: Treat symptomatically and supportively.

Section 5 - Fire Fighting Measures

General Information: As in any fire, wear a self-contained breathing apparatus in pressure-demand,

MSHA/NIOSH (approved or equivalent), and full protective gear. During a fire, irritating and highly toxic gases may be generated by thermal decomposition or combustion.

Extinguishing Media: Use water spray, dry chemical, carbon dioxide, or appropriate foam.

Flash Point: Not available.

Autoignition Temperature: Not available. Explosion Limits, Lower: Not available.

Upper: Not available.

NFPA Rating: (estimated) Health: 2; Flammability: 0; Instability: 0

Section 6 - Accidental Release Measures

General Information: Use proper personal protective equipment as indicated in Section 8.

Spills/Leaks: Clean up spills immediately, observing precautions in the Protective Equipment section. Sweep up or absorb material, then place into a suitable clean, dry, closed container for disposal. Avoid generating dusty conditions. Provide ventilation.

Section 7 - Handling and Storage

Handling: Wash thoroughly after handling. Remove contaminated clothing and wash before reuse. Use only in a well-ventilated area. Minimize dust generation and accumulation. Avoid contact with eyes, skin, and clothing. Avoid ingestion and inhalation.

Storage: Keep container closed when not in use. Store in a cool, dry, well-ventilated area away from incompatible substances. Keep containers tightly closed.

Section 8 - Exposure Controls, Personal Protection

Engineering Controls: Use adequate general or local exhaust ventilation to keep airborne concentrations below the permissible exposure limits.

Exposure Limits

Chemical Name	ACGIH	NIOSH	OSHA - Final PELs
. 3	Imatter containing no acheeres	I IO ma/m 3 IWA (fotal dilst): 5	ma/m 3 I W/W (rechirable

OSHA Vacated PELs: Calcium sulfate, anhydrous: 15 mg/m3 TWA; 5 mg/m3 TWA (respirable fraction)

Personal Protective Equipment

Eyes: Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166.

Skin: Wear appropriate protective gloves to prevent skin exposure.

Clothing: Wear appropriate protective clothing to prevent skin exposure.

Respirators: Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149.

Always use a NIOSH or European Standard EN 149 approved respirator when necessary.

Section 9 - Physical and Chemical Properties

Physical State: Powder

Appearance: colorless to white

Odor: odorless **pH:** Not available.

Vapor Pressure: Not available.

Vapor Density: 4.69

Evaporation Rate: Not available.

Viscosity: Not available. Boiling Point: Not available.

Freezing/Melting Point: 1450 deg C

Decomposition Temperature: Not available.

Solubility: slightly soluble

Specific Gravity/Density: 2.9600g/cm3

Molecular Formula:CaO4S Molecular Weight:136.14

Section 10 - Stability and Reactivity

Chemical Stability: Stable under normal temperatures and pressures.

Conditions to Avoid: Incompatible materials, moisture, strong oxidants.

Incompatibilities with Other Materials: Strong oxidizing agents.

Hazardous Decomposition Products: Oxides of sulfur, irritating and toxic fumes and gases.

Hazardous Polymerization: Has not been reported.

Section 11 - Toxicological Information

RTECS#:

CAS# 7778-18-9: WS6920000

LD50/LC50: Not available.

Carcinogenicity:

CAS# 7778-18-9: Not listed by ACGIH, IARC, NIOSH, NTP, or OSHA.

Epidemiology: No data available.
Teratogenicity: No data available.
Reproductive Effects: No data available.

Neurotoxicity: No data available.

Mutagenicity: No data available.

Other Studies: No data available.

Section 12 - Ecological Information

No information available.

Section 13 - Disposal Considerations

Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. US EPA guidelines for the classification determination are listed in 40 CFR Parts 261.3. Additionally, waste generators must consult state and local hazardous waste regulations to ensure complete and accurate classification.

RCRA P-Series: None listed. RCRA U-Series: None listed.

Section 14 - Transport Information

	US DOT	IATA	RID/ADR	IMO	Canada TDG
	No information available.				No information available.
Hazard Class:		•			
UN Number:					
Packing Group:					

Section 15 - Regulatory Information

US FEDERAL

TSCA

CAS# 7778-18-9 is listed on the TSCA inventory.

Health & Safety Reporting List

None of the chemicals are on the Health & Safety Reporting List.

Chemical Test Rules

None of the chemicals in this product are under a Chemical Test Rule.

Section 12b

None of the chemicals are listed under TSCA Section 12b.

TSCA Significant New Use Rule

None of the chemicals in this material have a SNUR under TSCA.

SARA

CERCLA Hazardous Substances and corresponding RQs

None of the chemicals in this material have an RQ.

SARA Section 302 Extremely Hazardous Substances

None of the chemicals in this product have a TPQ.

Section 313

No chemicals are reportable under Section 313.

Clean Air Act:

This material does not contain any hazardous air pollutants. This material does not contain any Class 1 Ozone depletors. This material does not contain any Class 2 Ozone depletors.

Clean Water Act:

None of the chemicals in this product are listed as Hazardous Substances under the CWA. None of the chemicals in this product are listed as Priority Pollutants under the CWA. None of the chemicals in this product are listed as Toxic Pollutants under the CWA.

OSHA:

None of the chemicals in this product are considered highly hazardous by OSHA.

STATE

CAS# 7778-18-9 can be found on the following state right to know lists: Pennsylvania, Minnesota, Massachusetts. California No Significant Risk Level: None of the chemicals in this product are listed.

European/International Regulations

European Labeling in Accordance with EC Directives Hazard Symbols:

XΙ

Risk Phrases:

R 36/37 Irritating to eyes and respiratory system.

Safety Phrases:

S 24/25 Avoid contact with skin and eyes.

WGK (Water Danger/Protection)

CAS# 7778-18-9: 0

Canada - DSL/NDSL

CAS# 7778-18-9 is listed on Canada's DSL List.

Canada - WHMIS WHMIS: Not available.

Canadian Ingredient Disclosure List

Exposure Limits

CAS# 7778-18-9: OEL-AUSTRALIA:TWA 10 mg/m3 OEL-BELGIUM:TWA 10 mg/m3 OEL-UNITED KINGDOM:TWA 10 mg/m3 (total dust) JAN9 OEL-UNITED KINGDO M:TWA 5 mg/m3 (resp. dust) OEL IN BULGARIA, COLOMBIA, JORDAN, KOREA c heck ACGIH TLV OEL IN NEW ZEALAND, SINGAPORE, VIETNAM check ACGI TLV

Section 16 - Additional Information

MSDS Creation Date: 9/23/1998 Revision #3 Date: 3/18/2003

The information above is believed to be accurate and represents the best information currently available to us. However, we make no warranty of merchantability or any other warranty, express or implied, with respect to such information, and we assume no liability resulting from its use. Users should make their own investigations to determine the suitability of the information for their particular purposes. In no event shall Fisher be liable for any claims, losses, or damages of any third party or for lost profits or any special, indirect, incidental, consequential or exemplary damages, howsoever arising, even if Fisher has been advised of the possibility of such damages.





Attachment 2

Project Example

Subject: Treatability Study Design for Trace Element Sequestration

From: Bernd W. Rehm Date: 9 May 2011

Project: Confidential Client

Introduction

Physical containment of groundwater containing a variety of trace elements is the proposed approach for stopping the discharge of these elements to Arthur Kill. Continuing groundwater flow into the contained area must be managed or released to prevent by-passing of the physical containment. Passive sequestration of the trace elements in permeable reactive gates is the preferred approach for the release of the groundwater.

The ReSolution Partners memorandum of 27 December 2010 identified eight constituents of concern (COCs) for remedial evaluation. It is assumed that the sequestration process will be applied to groundwater in the slag and fill. The groundwater in the deeper stratified drift above the Woodbridge Clay will not require remedial action. The spatial distribution and concentrations of the COCs varies significantly across the site. It is assumes that one reactive gate will be required in an area where COC concentrations are high (MW-8). The remediation goals (RGs) for the groundwater released to Arthur Kill and Cranes Creek have not yet been agreed to with the NJDEP. Proposed remediation goals in the 27 December memorandum and the maximum COC concentrations are as follows:

Constituent of Concern	Proposed Remediation Goal (µg/L)	Maximum Observed On-site Concentration in 2010 (µg/L)	Required In situ Maximum Concentration Reduction to Meet the Remediation Goal (%)
Antimony	640	1,000	36
Arsenic	880	8,800	90
Cadmium	200	2,000	90
Copper	32	180	90
Lead	24	110	78
Nickel	27	160	83
Selenium	360	3,600	90
Zinc	760	7,600	90

Proposed Remedial Approach

The groundwater in the slag and fill is aerobic (dissolved oxygen of 0 to 8.0 mg/L and oxidation reduction potential [ORP] of -140 to 180 mV) and has a slightly alkaline pH (6.9 to 9.5). Under these conditions the COCs are expected to be present as either oxyanions for antimony [Sb(OH)₆], arsenic [HAsO₄²⁻], and selenium [SeO₄²⁻] or as divalent cations for cadmium, copper, lead, nickel, and zinc. The cations may be complexed with hydroxide (OH⁻), carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), or chloride (Cl⁻) in the groundwater. Chloride complexation may be especially important on the east side of the Site where tidally influenced flows mix saline Arthur Kill waters with the groundwater.

The approach for sequestering the COCs is proposed to create reducing (anaerobic) conditions within the reaction gates. In the presence of sulfides all of the COCs but selenium can form insoluble sulfide minerals, which removes the COCs from the groundwater. Selenium does not combine with sulfide. Rather selenium will be reduced to a divalent anion, which will form insoluble metal-selenide minerals comparable to the sulfide sequestration process. The applicability of this approach is supported by on-site observation in the stratified drift below the slag and fill. In this portion of the groundwater flow system the conditions are anaerobic with ORP values -95 to -230 mV and COC concentrations are below the proposed remediation goals.

The goal of the current treatability study is to evaluate the choice of reducing agents, the efficacy of sulfide production, and the extent to which the sulfide and selenide will reduce the COC concentrations. Static, non-flowing, trials are planned for this stage of the treatability study. The reactive gate however will be a dynamic setting, with groundwater passing through the gate at some yet undefined rate. This groundwater flow rate will be defined by the site hydrogeology as simulated with a numerical flow model and the proposed gate dimensions. Once the groundwater flow rate through the gate has been estimated, the need for, and design of an addition treatability study to evaluate the sequestration process under flowing conditions will be evaluated. If deemed necessary and appropriate, additional studies using bench-scale columns or in-field pilot tests will be developed.

The proposed approach uses compost and zero-valent iron (ZVI), singly or in combination, for generating reducing conditions in shallow groundwater. Both materials are capable of lowering the ORP of the groundwater to levels at which the sulfur present in the groundwater is reduced to sulfate and the selenium is reduced to selenide. In an anaerobic setting sulfate present in the groundwater would be converted to sulfide in the reducing reaction wall. However, based on the groundwater sampling completed in 2010, the sulfate concentrations in the slag and fill groundwater (8 to 170 mg/L) may be too low to provide sufficient sulfur for sulfide generation. The proposed approach will therefore also address the need to add sulfur to the shallow groundwater to facilitate the sequestration process. In addition, compost such as wood waste, nut shells, vegetable waste, and leaves is capable of adsorbing a variety of metals.

Sample Collection

First Environment collected samples of site groundwater and slag in February 2011 as follows:

Slag	Groundwater
MW-8	MW-8
MW-15	MW-15S
	MW-15D

The samples were sent to ReSolution Partners for the treatability study where the slag was prepared as described below and placed under refrigeration until used in the tests.

Treatability Study Design

The treatability study was completed in the ReSolution Partners' Madison laboratory. Analyses of time- and oxygen-sensitive analyses was completed by ReSolution Partners while quantitative analyses of COCs and selected parameter analyses was completed by Environmental Science Corporation. Samples for testing were collected by First Environment.

The treatability study design is summarized in the following table, where each "X" indicates a sample for analysis:

Time	Compost	Compost+ZVI	ZVI	Control
(weeks)	$+SO_4$	$+SO_4$	+SO ₄ +Slag	
0				X
2	XX	XX	XX	X
4	XX	XX	XX	XX

The compost consisted of wood chips (70 percent by weight) and leaf litter/garden compost (30 weight percent). The material is inexpensive and expected to slowly degrade and provide reducing conditions over an extended period. The wood chip and litter compost was mixed with Madison, Wisconsin tap water and placed in containers approximately 8 weeks in advance of the treatability trials to initiate anaerobic conditions. A commercially available ZVI product was used in the trials (Hepure HCA-150N). ZVI was added to the compost to increase the reducing potential of the compost. Reagent-grade gypsum (CaSO₄·xH₂0) was used to provide a source of slowly dissolving sulfate.

Each trial (X) consisted of site groundwater mixed with the reagents described above. Slag was added to each trial to provide pH buffering that may be present in an *in situ* application and provide a substrate for the growth of microbes (literature suggests that sulfate reducing bacteria prefer attachment rather than free-floating). The water and

solids were placed in glass jars with tight-fitting lids. Teflon tape was placed on the jar threads and the caps were taped to minimize the potential for sample contamination by oxygen. The jars were kept at room temperature for the duration of the trials and mixed periodically by tumbling by hand. Once a jar was opened for testing and sampling as described below the sample was disposed.

The analytical program included the following:

Analyte	Test Method	Analyst
pН	Electrode (SW846	ReSolution Partners
	9045)	
ORP	Electrode	ReSolution Partners
Sulfide	Colorimetry (EPA	ReSolution Partners
	376.2)	
Ferrous iron	Colorimetry (ASTM	ReSolution Partners
	D 1068 – 77)	
COCs	ICP (SW846 6020)	ESC
Sulfate	Ion Chromatography	ESC
	(SW846 9056)	
Dissolved organic	(SW846 9060)	ESC
carbon (DOC)		

The pH, ORP, sulfide, and ferrous iron were measured immediately upon opening the trail jar. An aliquot was then be removed from the trail jar, filtered at 0.45 um, and preserved for analyses of COCs and DOC. Finally, the sulfate aliquot was withdrawn. The samples intended for analyses by ESC were be placed on ice and submitted under chain-of-custody to ESC. The ESC laboratory reports are provided in Appendix A.

Two trials are shown for week two. In the event that the first trial jar demonstrated insufficiently negative ORP, the second trial jar would have been utilized for a longer duration until the ORP levels would achieve sufficiently anaerobic conditions. Since the first trial jars indicated anaerobic conditions for the screening parameters, the contents of the second trial jar was submitted for laboratory parameter analysis. The double trials shown for week four (XX) indicate duplicate trails were tested. The results of the testing showed that the RGs were approached in the two-week trial and the four-week trial was completed as confirmation of the COC sequestration.

Results

The results of the COC sequestration trials are summarized in Table 1. The data are grouped by sample type beginning with the control samples and followed by the compost alone, the compost + ZVI, and the ZVI alone.

The control samples were alkaline and aerobic, with no dissolved sulfide or ferrous iron low sulfate, and low dissolved organic carbon (DOC) concentrations. The concentrations of the COCs in the control samples showed varying trends over the course of the study.

Arsenic, copper, lead, and selenium were relatively comparable over time. Cadmium, nickel, and zinc concentrations suggest a decrease in concentrations over time. Antimony showed variably increasing concentrations over time. The week two antimony results appear to be anomalous. The cause(s) for these changes are not known. Possible time-dependent reactions of the slag in the samples suggested by slight pH increases and ORP decreases resulted in antimony release and adsorption or precipitation of cadmium, nickel, and zinc. The changing control concentrations will be considered when assessing the sequestration trials.

Compost and gypsum (sample identification C-S-) made the groundwater more acidic and lowered the ORP by over 500 mV. The gypsum resulted in 1,400 mg/L of sulfate, which in turn was partially converted to sulfide. Ferrous iron was also produced by the anoxic conditions in the sample. When compared to the controls the compost-amended samples showed greater than about 90 percent concentration reductions in antimony, cadmium, copper, lead, and selenium. Slight reductions were noted for arsenic and zinc while nickel showed little to no concentration reduction. Only the nickel concentrations continued to slightly exceed the remediation goal. The concentrations reductions occurred within two weeks. Only arsenic suggests that longer reaction times (4 weeks) significantly improve the reduction in concentration.

Compost and gypsum plus ZVI (sample identification C-S-Z-) created more anaerobic conditions than compost alone, with corresponding higher sulfide and ferrous iron concentrations. The addition of ZVI also resulted in slightly lower concentrations of the COCs with the exception of nickel where the concentrations were comparable to compost alone. Arsenic concentrations again suggest that increased reaction times improve sequestration of arsenic.

ZVI alone (C-Z-) showed significantly better arsenic sequestration and slightly poorer selenium sequestration than the other treatments. The response of the other COCs was comparable to the compost-amended trails. Again, there was little to no nickel sequestration.

Conclusions

The compost and gypsum amended trials significantly reduced the concentrations of all COCs but nickel. The addition of ZVI to the compost did not improve the overall performance. By four weeks of reaction the both compost alone and compost plus ZVI provided comparable arsenic reductions.

Recommendations

Previous reports noted that the batch trials used in this study do not address issues of residence time within the proposed permeable reactive gates. The degree to which this is of concern to the overall remedy design depends upon the numerical simulations of reactive gates which will provide groundwater flow rates through and residence times within the reactive gates. The need for additional bench-scale column studies or in-field pilot tests to address the residence time question will be reviewed once the simulation data is available.

Table 1. Treatability Study Results

	Slag	GW		Reagents	(g)	Reaction Time		Screening P	arameters	
Sample ID	(g) (mL)		Compost	Calcium Sulfate	Zero Valent Iron	(weeks)	рН	ORP (mV)	Sulfide (mg/L)	Ferrous Iron (mg/L)
Cont	20	250	0	0.0	0.00	1	N/A	307	0.0	0.1
Cont-2	20	250	0	0.0	0.00	2	8.11	236	0.0	0.2
Cont-4 (Dup-1)	20	250	0	0.0	0.00	4	8.53 (8.59)	244 (84)	0.0(0.0)	0.0 (0.0)
C-S-2	10	250	30	2.0	0.00	2	7.33	-235	1.0	0.8
C-S-4 (DUP-2)	10	250	30	2.0	0.00	4	7.69 (7.74)	-235 (-212)	0.3 (0.4)	3.0 (2.0)
C-S-Z-2	10	250	30	2.0	0.50	2	7.80	-359	0.4	8.0
C-S-Z-4 (DUP-3)	10	250	30	2.0	0.50	4	7.72 (7.81)	-271 (-313)	0.2(0.1)	7.0 (9.0)
S-Z-2	30	250	0	2.0	0.50	2	7.76	-230	0.0	0.8
S-Z-4 (DUP-4)	30	250	0	2.0	0.50	4	7.73 (7.84)	-62 (-93)	0.0(0.0)	10 (0.8)
					Laboratory Pa	arameters (mg/L)				
Sample ID	Sulfate	Dissolved Organic Carbon	Antimony	Arsenic	Cadmium	Copper	Lead	Nickel	Selenium	Zinc
Cont	170	7.2	1.5	1.3	0.42	0.029	0.065	0.19	2.6	1.9
Cont-2	170	7.3	0.0032	1.3	0.15	0.028	0.033	0.046	2.7	0.20
Cont-4 (Dup-1)	160 (160)	7.2 (7.1)	7.2 (6.6)	2.4 (2.0)	0.055 (0.063)	0.022 (0.020)	0.039 (0.021)	0.024 (0.029)	2.7(2.7)	0.31 (0.038)
C-S-2	1400	34	0.042	1.0	0.0092	< 0.0020	0.0015	0.037	0.13	0.13
C-S-4 (Dup-2)	1400 (1400)	33 (27)	0.038 (0.054)	0.80 (0.73)	0.0054 (0.0047)	<0.0020 (<0.0020)	0.0018 (0.0012)	0.028 (0.031)	0.069 (0.055)	0.083 (0.044)
C-S-Z-2	1400	40	0.018	0.24	0.00062	< 0.0020	< 0.0010	0.038	0.042	0.049
C-S-Z-4 (DUP-3)	1600 (1600)	40 (42)	0.016 (0.018)	0.080 (0.092)	<0.00050 (<0.00050)	0.0062 (<0.0020)	0.0022 (<0.0010)	0.029 (0.29)	0.017 (0.17)	0.033 (<0.010)
S-Z-2	1600	6.3	0.0040	0.029	0.048	0.0099	0.012	0.048	0.49	0.21
S-Z-4 (DUP-4)	1600 (1700)	6.1 (6.0)	0.99 (0.99)	0.071 (0.031)	0.0073 (0.014)	0.0065 (0.0046)	0.0023 (<0.0010)	0.040 (0.041)	0.061 (0.033)	0.062 (0.17)
Remediation Goals			0.64	0.88	0.20	0.032	0.024	0.027	0.36	0.76

Bold and red entries indicate exceedance of a remediation goal.