Memorandum

To: Julie Rapoport, CalStar **Date:** July 28, 2009

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Subject: Metals Exposure Evaluation - Newly Manufactured CalStar Coal Fly Ash (CFA) Bricks

This memorandum presents an exposure evaluation of metals sampling data for newly manufactured CalStar Coal Fly Ash (CFA) bricks, performed in support of the first phase of a product exposure assessment. Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) results were evaluated to determine the leaching potential of CFA trace metals from fly ash bricks, and surface wipe sample results were evaluated to assess the potential for dermal and oral ingestion exposures (*via* hand-to-mouth contact) to CFA trace metals from direct skin contact with exterior bricks. Based on Gradient's evaluation of the sampling results, the presence of CFA metals in newly manufactured CalStar bricks is not expected to result in any exposures of health concern *via* dermal contact with brick surfaces or *via* leaching. Additional details regarding Gradient's exposure evaluation are provided below.

1 Sample Collection and Analysis

Newly manufactured brick halves were collected by CalStar on 6/22/2009 and were sent to two laboratories for analysis. ACZ Laboratories (Steamboat Springs, CO) performed TCLP and SPLP extractions and subsequent metals analysis. Torrent Laboratories, Inc. (Milipitas, CA) performed sampling and metals analysis of brick sample wipes.[1]

2 Quality Control Review

Prior to interpreting the sampling data, Gradient reviewed the quality control (QC) results associated with the brick sample analyses to determine whether any data quality issues would affect the validity of the reported data (note that raw data were not yet made available and thus were not reviewed). Our evaluation included a review of QC summary results for initial and continuing calibration verification samples (ICVs and CCVs) and blanks (ICBs and CCBs), method blanks, laboratory control

[1] As described in Gradient's Sampling and Analysis Plan (Gradient, 2009), both new and "aged" CFA brick samples will be evaluated by Gradient. The "aged" brick halves are currently being subjected to freeze-thaw testing according to ASTM Standard C 67. When the freeze-thaw testing is complete in 2-3 months, the "aged" brick halves will also undergo metals testing, at which time Gradient will perform a similar exposure evaluation as presented herein. A final report summarizing all of the results will be prepared for CalStar at this time.

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samples (LCS), analysis duplicates, matrix spike/matrix spike duplicates, ICP serial dilutions, *etc.* Based on the QC review, we determined that in general, the brick sample analyses were in control and the reported data were considered usable. Note that some of the data results were qualified during the QC review; for example, some of the antimony, arsenic, copper, selenium, and zinc wipe sample results, SPLP lead results, and TCLP nickel and zinc results were re-assigned as nondetects (qualified U) due to method blank contamination.[2]

3 Data Evaluation

3.1 Surface Wipe Samples

Torrent Laboratories, Inc. reported wipe sampling results in micrograms of metal per wipe (µg/wipe) and brick dimensions in mm (length, width, height, and hole diameter). Gradient calculated the surface area of each brick according to Equation 1, below. We then divided the laboratory results in µg/wipe by the surface area sampled in order to determine the surface wipe loading in micrograms of metal per square meter (µg/m^2):

$$\text{Surface Area} = 2(LW+LH+WH) - 4\pi(D/2)^2 \qquad \text{(Equation 1)}$$

L=Length H=Height
W=Width D=Hole Diameter

Once the surface wipe loading was determined, Gradient calculated the minimum, maximum, and mean wipe sample results, as well as the coefficient of variability (CV) for each metal. Nondetected results were replaced with one half of the reporting limit in order to calculate summary statistics. The associated summary statistics are shown in Table 1. As shown in Table 1, many of the metals of toxicological concern (*e.g.*, arsenic, beryllium, cadmium, selenium, thallium) were not detected in any surface wipe samples despite the use of highly sensitive analytical methods. Other metals (*e.g.*, barium, chromium, cobalt, lead, mercury, molybdenum, nickel, silver, vanadium) were consistently detected, with relatively low sample-to-sample variability (as reflected in the calculated CV values).

To assess the potential health significance of the surface wipe results, we compared detected values (and values equal to one-half the reporting limit for the metals that were not detected) to the World Trade Center (WTC) health-based settled dust screening values (COPC Committee, 2003). These screening values, which are based on conservative (*i.e.*, health protective) exposure assumptions (*e.g.*, every day exposures of young children over extended periods of time) and toxicological values, were developed by US EPA and other members of the Contaminants of Potential Concern (COPC) Committee of the World Trade Center Indoor Air Task Force Working Group to support residential cleanup efforts in Lower Manhattan following the World Trade Center catastrophe. They were developed to be protective of potential exposures associated with ingestion and dermal contact with contaminants in dust residues on indoor surfaces, and due to the incorporation of several assumptions specific to indoor exposure conditions (*e.g.*, exposure times of 4 hours/day for hard surfaces), represent highly conservative comparison criteria for exterior surfaces. Given that US EPA accounted for the dissipation of contaminant surface loadings in dust (which is expected for dust borne contaminants, when there is not

[2] Details regarding Gradient's QC review will be presented in the final report submitted to CalStar.

an active contaminant source, due to a combination of cleaning, resuspension, dilution, and volatilization) in the development of the WTC screening values, we also provide in Table 1 modified WTC screening values where there is no consideration of dissipation. These modified WTC screening levels are approximately 60% less than the published WTC screening values, and are considered to be more appropriate for comparison with the brick surface wipes where metals surface loadings are not expected to diminish with time in the same manner.[3]

Table 1 shows that all surface wipe results are well-below the WTC settled dust screening values (both with and without dissipation), indicating that regular dermal contact with newly manufactured CalStar fly ash bricks is not expected to result in any exposures of health concern.

Table 1
Summary of Wipe Sample Results (µg/m^2)

Analyte	N	N Detected	Minimum	Maximum	Average	CV	WTC Screening Level[1]	WTC Screening Level Without Dissipation
Antimony	5	0	12	18	15	0.16	627	261
Arsenic	5	0	16	23	21	0.15	387	163
Barium	5	5	2263	5377	4092	0.29	109,752	45,760
Beryllium	5	0	3	3	3	0.03	3,136	1,307
Cadmium	5	0	3	3	3	0.03	1,557	649
Chromium	5	5	35	78	57	0.29	4,704	1,961
Chromium, Hexavalent	5	5	14	74	33	0.76	4,704	1,961
Cobalt	5	5	14	44	31	0.35	31,358	13,074
Copper	5	0	60	107	85	0.25	62,716	26,149
Lead	5	5	13	34	25	0.32	270	NA
Mercury	5	5	1	3	2	0.35	157	65
Molybdenum	5	3	3	9	5	0.43	NA	NA
Nickel	5	5	25	81	52	0.39	31,358	13,074
Selenium	5	0	48	61	54	0.10	7,839	3,269
Silver	5	5	8	22	16	0.37	7,839	3,269
Thallium	5	0	3	3	3	0.03	110	46
Vanadium	5	5	83	208	156	0.31	10,975	4,576
Zinc	5	0	1039	2060	1458	0.33	470,366	196,116

Notes:
Nondetects were replaced with 0.5×Reporting Limit (RL). Note that in cases where the sample result was considered nondetected and qualified (U) due to blank contamination, the RL was raised to the concentration detected in the sample.
CV=coefficient of variation, NA=Not Available
[1] World Trade Center Indoor Air Task Force Working Group, Contaminants of Potential Concern (COPC) Committee. May 2003. "World Trade Center indoor environmental assessment: Selecting contaminants of potential concern and setting health-based benchmarks.".

[3] Note that there may be some reduction in surface metal loadings in the bricks over time due to washing away of metals in rainwater, and for some metals (*e.g.*, mercury) *via* volatilization. As a result, comparison with the modified WTC screening values may add to the conservatism in the evaluation of the surface wipe sampling results. Note that potential exposures associated with the washing away of metals over time from the bricks are addressed by the TCLP and SPLP leaching protocols for the newly manufactured and freeze-thaw bricks (see Section 3.2 below for the TCLP and SPLP results for the newly manufactured bricks).

3.2 TCLP and SPLP Analyses

ACZ Laboratories, Inc. reported the SPLP results in milligrams of metal per liter (mg/L). Gradient calculated the minimum, maximum, and mean SPLP results as well as the coefficient of variation (CV) for each metal. Nondetected results were replaced with one half of the method detection limit in order to calculate summary statistics. The summary statistics are shown in Table 2. For comparison, US EPA National Drinking Water Standards[4], including both primary (health-based) and secondary (based on aesthetic, cosmetic, or technical effects) standards, are also shown in Table 2.

Table 2
Summary of SPLP Results (mg/L)

Analyte	N	N Detected	Minimum	Maximum	Average	CV	US EPA Drinking Water Standard
Aluminum	5	5	20.1	23.6	21.84	0.070	0.05 to 0.2*
Antimony	5	5	0.00070	0.0012	0.00090	0.22	0.006
Arsenic	5	2	0.00025	0.0006	0.00037	0.45	0.01
Barium	5	5	0.52	0.741	0.6184	0.17	2
Beryllium	5	0	0.00005	0.00005	0.00005	0	0.004
Cadmium	5	0	0.00005	0.00005	0.00005	0	0.005
Chromium	5	5	0.07	0.0979	0.080	0.16	0.1
Cobalt	5	5	0.00033	0.00037	0.00034	0.049	NA
Copper	5	0	0.0015	0.0015	0.0015	0.0	1.3
Iron	5	2	0.0100	0.060	0.024	0.91	0.3*
Lead	5	0	0.00005	0.00030	0.00017	0.57	0.015
Manganese	5	0	0.0003	0.00025	0.00025	0	0.05*
Mercury	5	0	0.0001	0.0001	0.0001	0	0.002
Molybdenum	5	5	0.017	0.028	0.023	0.18	NA
Nickel	5	0	0.0003	0.0003	0.0003	0	NA
Selenium	5	5	0.013	0.015	0.014	0.062	0.05
Silver	5	0	0.0000	0.000025	0.000025	0	0.1*
Thallium	5	0	0.0001	0.00005	0.00005	0	0.002
Vanadium	5	5	0.020	0.029	0.024	0.16	NA
Zinc	5	0	0.005	0.005	0.005	0	5*

Notes:
Nondetects were replaced with 0.5×Method Detection Limit (MDL). Note that in cases where the sample result was considered nondetected and qualified (U) due to blank contamination, the MDL was raised to the concentration detected in the sample.
CV=coefficient of variation.
** denotes secondary drinking water standard. All other values are primary drinking water standards. See http://www.epa.gov/safewater/contaminants/index.html*
NA=Not Available.

[4] Available at the US EPA website: http://www.epa.gov/safewater/contaminants/index.html

ACZ Laboratories, Inc. also reported TCLP results in milligrams of metal per liter (mg/L). Gradient calculated the minimum, maximum, and mean TCLP result as well as the CV for each metal. Nondetected results were replaced with one half of the method detection limit in order to calculate summary statistics. These summary statistics are shown in Table 3. For comparison, the US EPA TCLP regulatory levels are also shown in Table 3[5].

Table 3
Summary of TCLP Results (mg/L)

Analyte	N	N Detected	Minimum	Maximum	Average	CV	TCLP Regulatory Level[1]
Aluminum	5	5	0.3	19.3	6.5	1.194	NA
Antimony	5	4	0.0010	0.0030	0.0022	0.38	NA
Arsenic	5	0	0.0015	0.0015	0.0015	0	5
Barium	5	5	0.8	1.7	1.1	0.329	100
Beryllium	5	0	0.00025	0.00025	0.00025	0	NA
Cadmium	5	0	0.00025	0.00025	0.00025	0	1
Chromium	5	5	0.10	0.12	0.11	0.063	5
Cobalt	5	5	0.0015	0.0020	0.0017	0.122	NA
Copper	5	0	0.0015	0.0015	0.0015	0	NA
Iron	5	0	0.01	0.01	0.01	0	NA
Lead	5	0	0.00025	0.00025	0.00025	0	5
Manganese	5	1	0.0015	0.004	0.002	0.559	NA
Mercury	5	0	0.0001	0.0001	0.0001	0	0.2
Molybdenum	5	5	0.030	0.036	0.033	0.069	NA
Nickel	5	0	0.0015	0.006	0.0024	0.839	NA
Selenium	5	5	0.023	0.030	0.026	0.1	1
Silver	5	0	0.00015	0.00015	0.00015	0	5
Thallium	5	5	0.0012	0.0019	0.0015	0.187	NA
Vanadium	5	5	0.012	0.032	0.020	0.38	NA
Zinc	5	0	0.005	0.01	0.007	0.391	NA

Notes:
Nondetects were replaced with 0.5×Method Detection Limit (MDL). Note that in cases where the sample result was considered nondetected and qualified (U) due to blank contamination, the MDL was raised to the concentration detected in the sample.
CV=coefficient of variation.
NA=Not Available
[1] See 40 CFR 264.24

[5] The TCLP limits are found in 40 CFR 264.21, downloaded at http://frwebgate.access.gpo.gov/cgi-bin/get-cfr.cgi?TITLE=40&PART=261&SECTION=24&TYPE=TEXT.

With the exception of aluminum in SPLP leachate, SPLP and TCLP results for each metal are below the respective comparison criteria, namely the US EPA National Drinking Water Standards and the US EPA TCLP regulatory levels. The SPLP results for aluminum exceed the secondary maximum contaminant level (MCL) range of 0.05 to 0.2 mg/L, but it is important to note that this secondary MCL is not health-based and instead is based on color changes. As a result, its exceedance does not indicate a potential exposure of health concern.[6] Therefore, based on the fact that no SPLP or TCLP leachate samples show exceedances of either the primary (*i.e.*, health-based) drinking water standards or the TCLP regulatory levels, we conclude that the leaching of metals from newly manufactured CFA bricks is not expected to result in exposures of health concern.

[6] Importantly, secondary MCLs are not enforced by US EPA and are only provided as guidelines for public water systems to assist them in their management of drinking water supplies for aesthetic considerations, such as taste, color, and odor. As such, they are not highly relevant for this exposure evaluation.

References

Gradient. 2009. Coal Fly Ash (CFA) Brick Sampling and Analysis Plan, Product Safety Testing/Exposure Evaluation Study. Prepared for CalStar Cement. June 8.

World Trade Center Indoor Air Task Force Working Group, Contaminants of Potential Concern (COPC) Committee. 2003. "World Trade Center indoor environmental assessment: Selecting contaminants of potential concern and setting health-based benchmarks." 78p. May.