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Potential for Recovery of Cerium Contained in Automotive Catalytic Converters

By Donald I. Bleiwas



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Cover. The left-hand photograph is of a typical stainless-steel-shelled catalytic converter used in motor vehicles. The right-hand photograph shows examples of the honeycomb structures (monoliths) contained in catalytic converters. The monoliths are composed of ceramic or stainless steel and coated with aluminum oxide, rare-earth oxides (most commonly cerium oxide), and platinum-group metals that may include palladium, platinum, and rhodium (Fornalczyk and Saternus, 2009). Photographs courtesy of Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc. Used with permission.

Contents

Introduction	1
Use of Cerium Oxide in Catalytic Converters	1
Amount of Cerium Oxide Contained in a Catalytic Converter	2
Recycling of Catalytic Converters	3
Total Contained Cerium Oxide and Potentially Recoverable Cerium Oxide Equivalents	4
Summary	6
References Cited	9

Figure

1. Stockpiled catalytic converters (CATCONs) that have been removed from vehicles before the CATCONs were dismantled and recycled for platinum-group metals..... 4

Table

1. Estimated amount of cerium oxide contained in catalytic converters in the United States in 2010 and potentially recoverable cerium oxide equivalents 7

Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
	Volume	
gallon (gal)	3.785	liter (L)
cubic inch (in ³)	16.39	cubic centimeter (cm ³)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	megagram (Mg); metric ton (t)
ton, long (2,240 lb)	1.016	megagram (Mg); metric ton (t)

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
	Volume	
liter (L)	0.2642	gallon (gal)
cubic centimeter (cm ³)	0.06102	cubic inch (in ³)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
megagram (Mg); metric ton (t)	1.102	ton, short (2,000 lb)
megagram (Mg); metric ton (t)	0.9842	ton, long (2,240 lb)

Potential for Recovery of Cerium Oxide Contained in Automotive Catalytic Converters

By Donald I. Bleiwas

Introduction

Catalytic converters (CATCONs) are required by Federal law to be installed in nearly all gasoline- and diesel-fueled onroad vehicles used in the United States. About 85 percent of the light-duty vehicles and trucks manufactured worldwide are equipped with CATCONs (Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc., written commun. July 10, 2012). These vehicles include buses, cars, light- and heavy-duty trucks, and motorcycles. Many offroad vehicles, such as trail bikes and all-terrain recreational vehicles, are also equipped with CATCONs, but offroad vehicles are not addressed in this paper (Manufacturers of Emission Controls Association, 2008).

Portions of the CATCONs (called monoliths) are recycled for their platinum-group metal (PGM) content and for the value of the stainless steel they contain. The cerium contained in the monoliths, however, is disposed of along with the slag produced from the recycling process. Although there is some smelter capacity in the United States to treat the monoliths in order to recover the PGMs, a great percentage of monoliths is exported to Europe and South Africa for recycling, and a lesser amount is exported to Japan. There is presently no commercial-scale capacity in place domestically to recover cerium from the monoliths.

Recycling of cerium or cerium compounds from the monoliths could help ensure against possible global supply shortages by increasing the amount that is available in the supply chain as well as the number and geographic distribution of the suppliers. It could also reduce the amount of material that goes into landfills. Also, the additional supply could lower the price of the commodity. This report analyzes how much cerium oxide is contained in CATCONs and how much could be recovered from used CATCONs.

Use of Cerium Oxide in Catalytic Converters

The purpose of a CATCON is to reduce the emission of harmful gases that are produced from the burning of fossil fuels, such as nitrogen oxides, carbon monoxide, and hydrocarbons. During the catalytic process, these gases are converted into nitrogen, carbon dioxide, and water.

A large surface area of catalytic material is necessary for CATCONs to operate effectively. To create this large surface area, manufacturers developed a honeycomb structure, referred to as a monolith, that is composed of ceramic or stainless steel and coated with aluminum oxide, rare-earth oxides (most commonly cerium oxide, which is also known as ceria), and PGMs that may include palladium, platinum, and rhodium. The PGMs in the CATCONs act as catalysts (Fornalczyk and Saturnus, 2009). The shape, size, and composition of monoliths vary by the total cylinder displacement of the engine, the fuel type used, and the manufacturer's design; however, in most cars and light-duty trucks, the monoliths measure about 10 centimeters (cm) in diameter and about 15 cm in length (Hilliard, 2004). In some cases, ceramic spherical beads are used instead of the honeycomb design.

Cerium is a rare-earth element that attracts oxygen and finds application in CATCONS as cerium oxide. Under high-oxygen conditions, the cerium oxide absorbs oxygen, which helps to increase the efficiency by which nitrogen oxide is reduced to nitrogen. Under low-oxygen conditions, the cerium oxide releases stored oxygen and increases the efficiency by which carbon monoxide is oxidized and becomes carbon dioxide (McCartney, 2003). The hydrocarbons are converted to water vapor and carbon dioxide (Spellman, 2009). Cerium allows the catalysts to operate at maximum efficiency as the air and fuel mixture in the engine is continuously cycled from slightly rich in oxygen to slightly poor in oxygen (Lenntech B.V., 2011; McCartney, 2003).

Amount of Cerium Oxide Contained in a Catalytic Converter

Data that quantify the actual cerium oxide content in CATCONS by vehicle type and model are not available, although a limited amount of generalized information is available. For this study, data were collected from literature and discussions with industry specialists. General content estimates from these sources ranged from 50 to 100 grams of cerium oxide per converter, but the estimates did not differentiate by the type of engine, whether the engine was diesel- or gasoline-fueled, or by the engine cylinder displacement, which are the leading determinants for cerium oxide loading (Kilbourn, 2000; McCartney, 2003; Uenishi and others, 2006; Bharali, 2009). The estimates developed for this study by category of vehicle, and the bases for these estimates, are discussed below and included in table 1.

Cars and Light-Duty Trucks.—Laboratory testing conducted in 2012 to determine the amount of cerium oxide in CATCONS installed in cars and light-duty trucks found the amount to be in the range of 75 grams of cerium oxide per converter (Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc., oral and written communs., May 1, 2012, and July 11, 2012, respectively). Pfefferle and Roychoudburi (1999) determined that a total weight of cerium oxide of at least 20 to 30 grams per liter of engine cylinder displacement is normally required for CATCONS. Applying this estimate to the weighted average engine cylinder displacement for cars and light-duty trucks for the period 1999 through 2010 results in an average weighted cylinder displacement of approximately 3.3 liters. In 2010, the average engine size for cars and light-duty trucks was also about 3.3 liters (U.S. Environmental Protection Agency, 2012). Using these data and the estimated amounts of cerium oxide required per liter of engine cylinder displacement results in a range of 66 to 99 grams of cerium oxide per converter for cars and light-duty trucks and is consistent with other estimates (Kilbourn, 2000; McCartney, 2003; Bharali, 2009; Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc., oral and written communs., May 1, 2012, and July 11, 2012, respectively). Based on these results, it was assumed for this study that cars and light-duty trucks had one CATCON and that each required 80 grams of cerium oxide (table 1).

Motorcycles.—Based on the 2009 Motor Cycle Industry Council Survey, which is the most recent survey performed by the group, the weighted average engine size of on-highway motorcycles and scooters was 900 cubic centimeters (cc) (Pat Murphy, Vice President, Research and Technology, Motorcycle Industry Council, oral and written communs., July 5, 2012). Assuming the same ratio of cerium oxide in CATCONS to engine cylinder displacement used for cars and light-duty trucks of 20 to 30 grams per liter and an average engine cylinder displacement of 900 cc per motorcycle, approximately 18 to 27 grams of cerium oxide would be required per CATCON per motorcycle. For this study, it was assumed that the CATCONS installed on each motorcycle contained 23 grams of cerium oxide (table 1).

Heavy-Duty Vehicles.—No information was available regarding the amount of cerium oxide contained in heavy-duty vehicles, such as buses and trucks, but they represent less than 5 percent of all registered vehicles that were in use, scrapped, or sold as new in 2010 (Davis, Diegel, and Boundy, 2011). It was assumed for this study that each CATCON installed on heavy-duty vehicles contained

100 grams of cerium oxide because they generally have larger engines than those installed in cars and light-duty trucks (table 1).

Aftermarket Sales.—The most common reasons for original equipment manufacturer (OEM) CATCONs to be replaced are the failure of the device to meet emission standards during inspection, damage to the CATCON, or theft of the CATCON. Most of the OEM CATCONs that were replaced were likely recycled to recover their PGM content. National statistics on the aftermarket sales of CATCONs were not available; however, it was reported that 880,000 new aftermarket CATCONs were sold in California during 2007 (Ozone Transport Commission, 2011). Based on the sales data in California, it can be grossly estimated that 2.5 million new aftermarket CATCONs containing 80 grams of cerium oxide in each converter were installed in vehicles in 2010. This number of aftermarket CATCONs represents less than 1 percent of the fleet of vehicles in use in the United States in 2010 (table 1; National Automobile Dealers Association, 2011).

Recycling of Catalytic Converters

Historically, the primary incentive to recycle CATCONs has been the revenues generated from the recovery of high-value PGMs contained in the monoliths. The value of scrapped CATCONs varies based primarily on the type and amount of PGM recovery, but on average in 2010, scrap dealers paid \$75 to \$250 per CATCON recovered from automobiles and trucks (CBS News, 2009; TundraHeadquarters.com, 2010). The amounts and proportions of PGMs required per CATCON vary but generally range from 2 to 6 grams of PGM per vehicle for cars, light-duty trucks, and motorcycles and 6 to 30 grams of PGM for vehicles with larger engines, such as sport utility vehicles and trucks (Wilburn and Bleiwas, 2005). CATCONs installed in vehicles equipped with diesel engines use platinum and rhodium; gasoline-powered vehicles generally use palladium, platinum, and rhodium.

In 2010, about 20 million CATCONs were dismantled in North America, and about 45 percent of these CATCONs were imported (Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc., oral and written commun., May 1, 2012, and July 11, 2012, respectively). A-1 Specialized Services & Supplies, Inc., which is located in Croydon, Pennsylvania, is the leading collector and processor of salvage automotive CATCONs in the world (A-1 Specialized Services & Supplies, Inc., 2012). This company, like other domestic recyclers, is actually a consolidator; the company collects, stockpiles, and dismantles the CATCONs to separate the monolith from the stainless steel converter shell that surrounds it (see fig. 1). The stainless steel converter shells are recycled offsite. Although there is some capacity in North America to process the monoliths at BASF Corp.'s several plants in Michigan and South Carolina, Stillwater Mining Co.'s smelter in Columbus, Montana, and PMR Refiner's precious-metal refinery in Boisbriand, Quebec, Canada, more than 75 percent of the monoliths are shipped to Europe and South Africa, where they are crushed, ground, and treated to recover the contained PGMs onsite; a lesser percentage is shipped to Japan (American Recycler, 2009; Missoulian, 2010; BASF Corp., 2012; Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc., written commun., July 19, 2012).



Figure 1. Stockpiled catalytic converters (CATCONs) that have been removed from vehicles before the CATCONs were dismantled and recycled for platinum-group metals. Photograph courtesy of Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc. Used with permission.

Roughly 70 percent or more of the contained PGMs are recovered through the recycling process. The recovery of PGMs from CATCONs is addressed in a study by Wilburn and Bleiwas (2005). In addition, A-1 Specialized Services & Supplies recently began smelting a portion of its own production at its Swindon, United Kingdom, facility (Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc., written commun., July 19, 2012).

Cerium oxide is not commercially recovered from CATCONs; instead, it is sent to landfills along with the waste produced by processing the monoliths for their PGM content. The end-of-year price of 96-percent-purity cerium oxide remained under \$20 per kilogram for more than a decade until 2006 when the end-of-year price first rose to \$40 per kilogram. The price increased to \$50 per kilogram at yearend 2007 and 2008 and then decreased to \$30 per kilogram at yearend 2009 and 2010. At yearend 2011, the price for the material reached \$60 per kilogram but dropped significantly in 2012 (U.S. Geological Survey Minerals Yearbook, various years; Joseph Gambogi, Mineral Commodity Specialist, U.S. Geological Survey, oral and written commun., June 27, 2012, July 5, 2012, and February 12, 2013, respectively). The higher price of cerium oxide for the years since the end of 2006 reflects a general increase in demand and, in 2011, a reduction in China's export quotas. (China provides more than 80 percent of the world's supply of cerium oxide.) Because of the relatively high price of cerium oxide and concerns that supply shortages could produce further price increases, research to investigate the profitable recovery of cerium oxide from CATCONs is ongoing (Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc., oral and written commun., May 1, 2012, and June 12, 2012, respectively).

Total Contained Cerium Oxide and Potentially Recoverable Cerium Oxide Equivalents

As noted previously, statistical data on the number of CATCONs dismantled in the United States and the number of units exported to be recycled elsewhere are not available; however, based on

discussions with industry experts and the limited statistical data available, it can be estimated that roughly 20 million monoliths may have been recovered from CATCONs in North America in 2010 and that about 45 percent of these CATCONs were imported (Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc., oral and written communs., May 1, 2012, and July 11, 2012, respectively). Virtually all the monoliths were then sent to smelters outside of the United States for recovery of the PGMs they contain.

The data in table 1 provide a perspective on the total amount of cerium, expressed as cerium oxide equivalents, that was potentially recoverable in CATCONs that were generated in the United States in 2010, including those that were (a) installed in cars and light-duty trucks, heavy-duty vehicles, and motorcycles in use in 2010; (b) installed in new cars, light-duty trucks, heavy-duty vehicles, and motorcycles sold in 2010; (c) obtained from cars and light-duty trucks scrapped in 2010; and (d) contained in OEM CATCONs replaced in 2010 because of the failure of the device to meet emission standards during inspection, theft, or exhaust system failure or loss.

The CATCONs installed on the exhaust systems of the small engines used in hybrid vehicles were not considered separately in the estimates but are assumed to be in the U.S. Environmental Protection Agency's estimates of average engine size (U.S. Environmental Protection Agency, 2012). Damaged and defective CATCONs that were produced by the manufacturers of the devices and by auto manufacturers but were sent directly to recyclers were also not considered in the estimates. The estimated tonnages, reported as cerium oxide and cerium oxide equivalents, are expressed to two significant figures to reflect the confidence level of the data.

The data indicate that roughly 19,000 metric tons of cerium oxide was contained in the CATCONs installed in the fleet of 250.2 million on-highway cars and light-duty trucks, heavy-duty vehicles, and motorcycles in use in the United States in 2010. Nearly 1,000 metric tons of cerium oxide was used for the nearly 15 million CATCONs installed in new vehicles sold and contained in after-market replacements in 2010. For comparison, about 1,770 metric tons of cerium oxide equivalents contained in numerous types of cerium compounds was imported into the United States in 2010 (U.S. Geological Survey, 2012). The amount of this material used in the domestic manufacture of CATCONs is confidential.

The estimated amount of cerium oxide contained in CATCONs in the 10.63 million cars and light-duty trucks reported as scrapped in 2010 and the 2.5 million CATCONs that were potentially part of the waste stream generated by their failure, theft, and other sources amounted to approximately 1,000 metric tons. Data on the scrapping of heavy-duty vehicles and motorcycles were not available and probably are not statistically important. The estimated number of vehicles designated as scrapping is based on data supplied by States that indicate the number of registered vehicles with major damage—from an accident or flood, for example—and those vehicles that have not been registered within a period of 1 year. It is not an estimate of the number of vehicles that enter the recycling stream by being dismantled for parts or shredded; that information was not available. If a vehicle is re-registered, it is added back to the approximation of the number of vehicles in use (National Automobile Dealers Association, 2011). Some of these vehicles, and the CATCONs installed in them, may not be available for recycling if they are exported out of the country, remain idle, or are placed back into service.

The estimates shown in table 1 of the amount of cerium oxide equivalents potentially recoverable from the recycling of CATCONs (assuming one CATCON per vehicle) are based on (a) a 70-percent efficiency in the collection of recyclable CATCONs, which is the fraction currently estimated for the United States, and (b) the results of bench-scale experiments that yield an estimated recovery of 70 percent of the cerium contained in the monoliths of CATCONs (Ashok Kumar, Director, A-1 Specialized Services & Supplies, Inc., oral and written communs., June 12, 2012, and

June 26, 2012, respectively). The data indicate that approximately 9,500 metric tons of cerium oxide equivalents was potentially recoverable from the in-use fleet of cars and light-duty trucks, heavy-duty vehicles, and motorcycles in 2010; that 480 metric tons was potentially recoverable from vehicles sold and replacement CATCONs installed; and that 520 metric tons was potentially recoverable from scrapped vehicles, replaced CATCONs, and other sources based on the estimate that each converter contained 80 grams of cerium oxide.

Summary

Although PGMs are routinely recovered through the recycling of CATCONs, there are currently no commercially viable technologies to recover the cerium content of CATCONs. At present, most of the world's scrapped CATCONs are dismantled in the United States by consolidators, but there is little domestic smelting capacity to treat and recover the PGMs and, potentially, the cerium they contain. Instead, more than 75 percent of the monoliths from the scrapped CATCONs are exported overseas for processing.

There are approximately 19,000 metric tons of potentially recoverable cerium oxide equivalents in CATCONs of the vehicle fleet currently in use in the United States, from which some portion becomes available as vehicles are retired or CATCONs are replaced. Assuming a collection efficiency of 70 percent for the CATCON recycling industry from domestic sources for the purpose of PGM recovery, roughly 770 metric tons of the 1,100 metric tons of cerium oxide equivalents contained in all retired vehicles and CATCONs from other domestic sources were placed in landfills in 2010. Based again on an assumed CATCON collection efficiency of 70 percent and a hypothetical 70-percent process recovery, approximately 520 metric tons of cerium oxide equivalents with a yearend value of about \$15 million was potentially available from scrapped vehicles, replaced CATCONs, and other sources in 2010. About 980 metric tons of cerium oxide was used in CATCONs installed in new vehicles and replacement CATCONs sold in 2010.

In the future, recovery of cerium from the monoliths could help reduce the United States' vulnerability to supply shortages by increasing the domestic supply of cerium and the number of supply sources of this rare earth while at the same time bringing commercial benefit and reducing the amount of material placed in waste facilities. Even with recovery of cerium in some form, however, the recycling of CATCONs will continue to rely on the economic viability of recovering their PGM content.

Table 1. Estimated amount of cerium oxide contained in catalytic converters in the United States in 2010 and potentially recoverable cerium oxide equivalents.

[Estimates are based on one catalytic converter per vehicle. Calculated estimates for cerium oxide and cerium oxide equivalents are rounded to two significant figures. CATCON, catalytic converter]

Source category	Number of vehicles ¹ (millions)	Amount of cerium oxide per catalytic converter (grams)	Total amount of contained cerium oxide (metric tons)	Amount of potentially recoverable cerium oxide equivalents ² (metric tons)
Vehicles in use in 2010: ³				
Cars and light-duty trucks	230.4	80	18,000	8,800
Heavy-duty vehicles	11.62	100	1,200	590
On-highway motorcycles	8.212	23	190	93
Total	250.2		19,000	9,500
New vehicles and CATCONs sold in 2010:				
New cars and light-duty trucks ⁴	11.39	80	910	450
New heavy-duty trucks ⁵	0.379	100	40	20
New on-highway motorcycles ⁶	0.307	23	7.1	3.5
New aftermarket CATCONs ⁷	2.5	80	20	9.8
Total	14.58		980	480
From scrap and other sources in 2010:				
Cars and light-duty trucks scrapped ⁸	10.63	80	850	420
CATCONs from replacement and other sources ⁷	2.5	80	200	98
Total	13.13		1,100	520

¹Rounded to the nearest thousand, except for new aftermarket CATCONs, which was rounded to two significant figures.

²Estimate based on 70-percent capture of CATCONs recovered from vehicles classified as scrappage and 70-percent metallurgical recovery. Scrapped vehicles were defined by the National Automobile Dealers Association as those vehicles no longer registered from a previous year. Vehicles may be re-registered at a later time, exported, or delivered to parts and scrap dealers.

³Source: U.S. Department of Transportation, Research and Innovative Technology Administration, 2011.

⁴Source: WardsAuto.com, 2012.

⁵Source: Davis, Diegel, and Boundy, 2011.

⁶Source: Chung, 2012.

⁷National statistics on the aftermarket sales and recycling of CATCONs were not available; however, it was reported that 880,000 new aftermarket CATCONs were sold in California during 2007 (Ozone Transport Commission, 2011). Based on the sales data in California, it can be grossly estimated that 2.5 million new aftermarket CATCONs containing 80 grams of cerium oxide in each converter were installed in vehicles in 2010 and that an equal number became potentially available for recycling.

Table 1. Estimated amount of cerium oxide contained in catalytic converters in the United States in 2010 and potentially recoverable cerium oxide equivalents.—Continued.

⁸Scrappage is defined as the number of registered vehicles with major damage—from an accident or flood, for example—and vehicles that have not been registered within 1 year. If a vehicle is re-registered, it is added back to the approximation of the number of vehicles in use (National Automobile Dealers Association, 2011). Some of these vehicles, and the CATCONs installed in them, may not be immediately available for recycling if they are exported out of the country, remain idle, or are placed back into service. The estimate does not represent the actual number of vehicles that enter the recycling stream by being dismantled for parts or shredded; that information was not available. Statistical data related to scrappage of heavy-duty vehicles and motorcycles were also not available.

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